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Optimization of dissolved heavy metals removal using sulfate-reducing bacteria in the upflow anaerobic fixed film reactor.

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Optimization of Dissolved Heavy Metals Removal Using Sulfate Reducing Bacteria in the Upflow Anaerobic Fixed Film Reactor

A Thesis Submitted to the
Faculty of Graduate Studies and Research
Through the Department of Environmental Engineering
in Partial Fulfillment of the Requirements for the
Degree of Master of Applied Science
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by

Syenny Chatrine Wijaya

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ABSTRACT

Upflow anaerobic fixed film reactor (UAFFR) dominated with sulfate reducing bacteria (SRB) is very effective in treating wastewater containing high concentration of heavy metals. SRB are able to reduce sulfates to sulfides. The sulfides would then react with metals to produce the metal sulfide precipitates. Therefore, maximizing the sulfide production is important in optimizing the filter performance. The maximum sulfide production was achieved at a lactate (organic source) loading of 6 kg/d/m3 and a phosphate addition of 0.18 g/L. The overall average consumptive ratio of the filter is 1.2, which indicates that 17% of organic used is for cell synthesis, and 83% for reduction and deoxygenation.

The filter is able to remove the total metals with efficiencies of : 60%-70% for Pb, 20%-70% for Cd; 80% for Cr; and 90% for Cu. The dissolved metal removal efficiencies are: 80% up to 45 mg/L Cr; >90% up to 18 mg/L Pb; >90% up to 400 mg/L Cu; and 99% up to 550 mg/L Cd. The filter has a higher dissolved metal removal efficiencies than the total metal removal efficiencies.

The behaviour of the Control Reactor indicates that sulfide precipitation is not the only mechanism in removing the dissolved heavy metals in the filter. Hydroxide and carbonate precipitations and chelations by organic and inorganic ligands are the other processes. Therefore, both the bacterial and non-bacterial dissolved metal removals occur in the filters.

The bacterial dissolved metal removals include sulfide and carbonate precipitations, because sulfide and carbonate are the

products of SRB. The bacterial metal removal efficiencies are: 80% Cu, 80% Cd and 60% Cr. The maximum limits of the heavy metal concentrations which the filter can treat satisfactorily without affecting SRB's growth are: 60 mg/L Cu, 550 mg/L Cd and 45 mg/L Cr.

To my Grandparents,

for their love and support.....

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I. INTRODUCTION

1.0 General

High concentrations of heavy metal have been known to be toxic and carcinogenic to living organisms. These can also cause serious problems in a biological waste treatment system. Therefore, their discharge to the environment poses a serious problem if not handled properly. In order to minimize the problem, the government sets standards of maximum metal concentrations that are allowed to be directly discharged to the water streams, as shown in Table 1.1.

Table 1.1
The limits to concentrations of heavy metals discharged to streams according to Ontario Ministry of the Environment (MOE)

Metals	Concentration (mg/L)
Cadmium	0.0001
Chromium	1.0
Copper	1.0
Lead	1.0
Nickel	1.0
Zinc	1.0

Metal plating is one of the industries which produces high metal concentrations in their wastewaters. As a result, it has become important to optimize its wastewater treatment for metal removal. There are different ways to remove the heavy metals. The main factors to be considered in choosing the treatment methods are

economic consideration, availability of raw materials and regulatory requirements.

Basically, there are two techniques for metal removal, recovery and solid removal. Recovery techniques are treatment methods used for the purpose of recovering or regenerating process constituents which would otherwise be lost in the wastewater or discarded [Cherry, 1982]. Included in this group are evaporation, ion-exchange, electrolytic recovery, electrodialysis and reverse osmosis.

Solid removal techniques are employed to remove metals and other pollutants from process wastewaters, to make the water suitable for reuse or discharge. These methods include hydroxide and sulfide precipitation, sedimentation, diatomaceous earth filtration, membrane filtration, granular bed filtration, peat adsorption, insoluble starch xanthate treatment and flotation [Cherry, 1982]. The most common and successful method of reducing heavy metal concentrations in solutions is chemical precipitation [McAnally et al., 1984; McFadden et al., 1985]. Most metals are relatively insoluble as hydroxides, carbonates or sulfides and can be precipitated in one of these forms [McAnally et al., 1984].

The most common form is hydroxide precipitation in which lime or caustic is added to the wastewater to produce an alkaline pH. The metal hydroxide precipitates are thus formed and settled down, and a supernatant with a low metal concentration is produced. However, problems are frequently encountered when hydroxide precipitation is used for metal removal [Cherry, 1982; Eisenberg et

al., 1985; McAnally et al., 1984; McFadden et al., 1985]. These include:

1. Large sludge volumes and poor filterability because of the gelatinous nature of metal hydroxide;
2. Excessive chemical cost because of the necessity for wastewater neutralization;
3. Reduction of Cr(VI) to Cr(III) must be accomplished prior to neutralization;
4. Theoretical minimum solubilities for different metals occur at different pH values;
5. Because hydroxide precipitates tend to resolubilize if the solution pH is increased or decreased from their minimum solubility points, maximum removal efficiency will not be achieved unless the pH is controlled within a narrow range;
6. The presence of complexing ions, such as phosphates, tartrates, EDTA and ammonia, that are commonly found in cleaner and plating formulations, may have an adverse effect on metal removal efficiencies.

Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation for removing various heavy metals. Some advantages of sulfide precipitation are [Cherry, 1982; Eisenberg et al., 1985; McAnally et al., 1984; McFadden et al.,

1985]:

1. Good removal efficiency can be expected with metal sulfides because of their low solubilities (Table 1.2);
2. Sulfide has the ability to remove chromate and dichromates without requiring the reduction of chromium to its trivalent state;
3. Sulfide will precipitate metals complexed with the most complexing agents;
4. Sulfide precipitates exhibit less of an amphoteric nature than hydroxide precipitates, and have a less tendency to resolubilize;
5. Studies show lower sludge volumes with sulfide treatment than with hydroxide treatment.

Disadvantages of this treatment include [Eisenberg et al., 1985]:

1. Hydrogen Sulfide generation;
2. The cost of sulfide precipitation is higher than the cost of lime precipitation.

Table 1.2
Solubility Product Constants of Metal Sulfides [Cherry, 1982]

Compounds	**Ksp**
Nickel Sulfide	1.4×10^{-24}
Lead Sulfide	3.4×10^{-28}
Cadmium Sulfide	3.6×10^{-29}
Copper Sulfide	8.5×10^{-45}

An alternative to reducing the high cost of chemical sulfide precipitant is to use anaerobic sulfate reducing bacteria (SRB) to produce the precipitant in the reactor. A study conducted by Wong et al. (1985) attempted to remove heavy metals from sewage sludge by utilizing sulfide oxidizing and sulfate reducing bacteria. Sulfide oxidizing bacteria will solubilize the heavy metals from the sludge and in turn the sulfate reducing bacteria will precipitate the metals from the wastewater (see Figure 1.1). The metal removal efficiency from the wastewater is very high, greater than 90%.

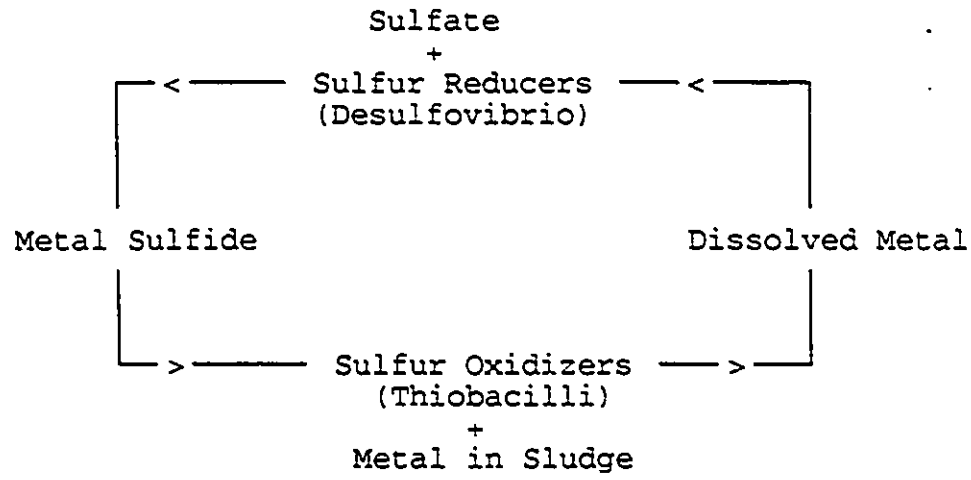


Figure 1.1
Biological sulfur reduction/sulfide oxidation process and their relationship to metals

1.1 Objective

The objective of this research is to investigate the removal of selected heavy metals from the wastewater using sulfate reducing bacteria (SRB) in the upflow anaerobic fixed film reactor (UAFFR)

and to optimize the filter's performances. The optimization of the filter's performances is done with respect to the sulfide production. Sulfide is the major compound that removes the metal by precipitating it as metal sulfide. The study also focuses on finding the maximum loading of heavy metals that the sulfate reducing bacteria (SRB) can tolerate, without sacrifying removal efficiencies.

1.2 Scope

The scope of the study involves:

(1) Establishing the organic loading required by SRB to produce the highest concentration of sulfide precipitant;

(2) Studying the importance of nutrients (phosphates) to the SRB performance, thus to the metal removal efficiency;

(3) Establishing the maximum limit of the heavy metals (Cu, Cr, Pb, Cd) loading which the filter can treat satisfactorily without affecting SRB's growth.

(4) Determining the efficiencies of soluble metal precipitation at different metal loading rates;

(5) Determining the efficiencies of total metal removal by the upflow anaerobic fixed film reactor (UAFFR).

II. LITERATURE REVIEW

It has been known that metal laden industrial wastewater poses potential adverse health effects and environmental impacts. These metals may be present both in solution and in suspension. This has led to the investigation of possible ways to remove the heavy metals from the wastewaters, prior to discharging them to natural water bodies.

Elenbogen et al. (1985) and Ming H. Cheng et al. (1975) studied the heavy metals uptake by activated sludge. Cheng reported that activated sludge treatment reduced influent levels of iron, copper, lead, nickel and zinc by 30% to 90%. At lower metal concentrations, metals were taken up by the biofloc through the formation of metal-organic complexes. At higher metal concentrations, metal ion precipitations from solution might occur in addition to sludge uptake [Cheng et al., 1975].

DeWalle (1979) studied heavy metal removals with a completely mixed anaerobic filter. According to DeWalle, the total metal removals in the filter were a function of the rate of inflow, hydraulic detention time and loading rate of the filter. Total metal removals generally decreased when the hydraulic detention time (HRT) decreased due to the increase in suspended solids and associated metals in the effluent. However, soluble metal removals were independent of the reactor's HRT. Chian et al., (1983) observed high soluble metal removals at a short detention time. It was concluded that the metals were precipitated as sulfides,

carbonates and hydroxides. DeWalle added that, at pH of less than 7, the sulfides determined the soluble heavy metal concentrations. Carbonates determined the soluble concentrations at higher pH.

Rivera (1983) investigated heavy metal removals in a packed bed anaerobic upflow (ANFLOW) bioreactor. Removal efficiencies for soluble zinc were greater than 95% when the influent concentration was 100 mg/L, about 90% for 300 mg/L and about 85% for 1000 mg/L.

Lappan (1987) studied the heavy metal removals using sulfate reducing bacteria (SRB) in the upflow anaerobic fixed film reactor. SRB was able to generate sulfides which would react with heavy metals to produce metal sulfide precipitates. It was found that soluble metal removal efficiencies were not a function of HRT when excess sulfides were present. However, total metal separation efficiencies depended on the reactor's HRT. Total metal removals in terms of separation efficiency were Cu > Zn > Ni > Pb.

Karhadkar [24] noted that the methanogenesis was noncompetitive with sulfate reduction when sulfate ions were abundant in the medium. Two stages of inhibition of methanogenesis thus existed as a result of sulfate reduction: primary inhibition due to competition for substrate from SRB; and secondary inhibition resulting from the decline of methanogenic population due to direct inhibition of cells' functions by soluble sulfides (Karhadkar et al., 1987; Parkin et al., 1990).

SRB's dominance over other bacteria, such as methanogens, and their ability to remove heavy metals had made them a favourable subject in the anaerobic filter to treat wastewater with high

concentration of heavy metals. However, heavy metals themselves were toxic to anaerobic bacteria. The toxicity of heavy metals depended on their concentration in the soluble or ionic form, and not on the total concentration in the digester (Lawrence et al., WPCF, 37, 3). Sulfides as the product of SRB respiratory process would precipitate heavy metals, thus reducing if not eliminating the toxic effect of ionic heavy metals.

Hayes et al. (1978) demonstrated the ability of bacteria to concentrate metal ions around the cell walls through complexation with proteins and acid groupings that served as binding sites. Thus, microbial uptake assisted sulfide precipitation in removing heavy metals from the wastewater supernatant.

Furthermore, SRB could also treat wastewater containing high sulfates. Sulfate, acting as an electron acceptor, was an important compound for SRB to produce sulfide. Maree et al. (1985) proposed that a possible way of increasing the sulfate reduction rate was by making use of a packed bed, instead of a completely mixed reactor, due to its larger surface area. It was believed that the larger the surface area, the higher would be the exposure of micro-organism to the sulfate-rich medium. Guiot et al. (1985) supported Maree's proposal of using a packed bed. According to Guiot, the loading capacities of an anaerobic wastewater treatment system were essentially dictated by the amount of active biomass that could be retained in the reactor, while maintaining sufficient contact between active biomass and wastewater. Meanwhile, Fiebig et al. (1985) showed that the biomass could be fixed very effectively on

a packing material of plastic rings.

Different types of anaerobic filter were used mostly for organic reduction and methane production. Kennedy et al. (1987) developed a downflow anaerobic fixed film reactor (DAFFR), while Maree et al. (1985) used upflow packed bed reactor to remove sulfate. Guiot et al. (1985) combined upflow anaerobic fixed film reactor [UAFFR] with upflow anaerobic sludge blanket reactor (UASBR) to treat sugar wastewater. However, in the comparative study of the UAFFR, DAFFR and UASBR, the UAFFR was found to be less sensitive to inhibitors, lower temperatures and load fluctuations [Lappan, 1987). These observations were based primarily on the reactor's ability to retain biomass by allowing it to fix and accumulate on the packing material within the reactor. The comparative study was supported by Young et al. (1989). Young found that greater efficiencies could be obtained in the upflow units than in downflow units when operated at the same organic loadings.

III. BACKGROUND

3.0 General

Wong et al. (1985) have shown that the existence of sulfur bacteria in an aqueous environment creates a microbial ecosystem (Sulfuretum). In the anoxic zone, the sulfates are reduced to sulfides by sulfate reducing bacteria (SRB). Above the anoxic zone, in the presence of oxygen, chemosynthetic and photosynthetic sulfide oxidizing bacteria convert the dissolved sulfides back to sulfates, as shown in Figure 3.1. Thus, in order to prevent conversion of sulfides back to sulfates, the system ought to be anaerobic.

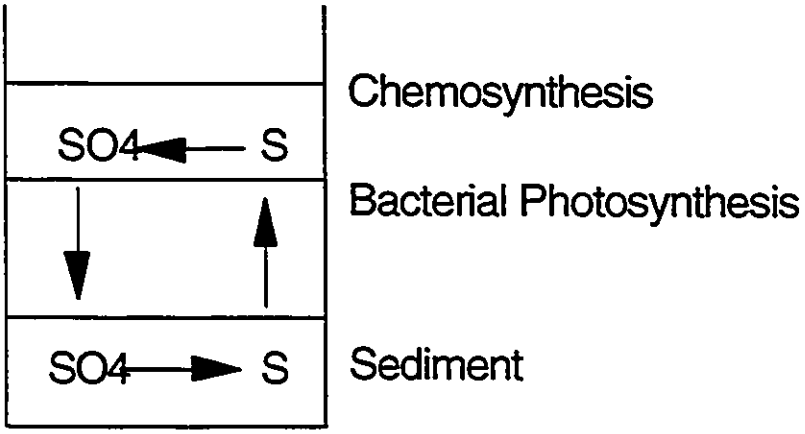


Figure 3.1
Microbial Ecosystem (Sulfuretum) [Wong et al., 1985]

The development of an anaerobic environment depends essentially on two conditions: (i) continued supply and degradation of organic matter, and (ii) limitation of air by physical means

[Pfennig et al., 1982]. The anoxic zone has a very low oxygen level, which satisfies the criteria for SRB to grow.

In an ecosystem as above, sulfides can precipitate metals as metal sulfides in the anoxic zone. The metal sulfides will remain in the sediment as long as the reducing environment is maintained [Wong et al., 1985]. On the other hand, under aerobic conditions, the metal sulfides will be oxidized by sulfide oxidizing bacteria, causing resolubilization of heavy metals.

The SRB reduce sulfates to sulfides. The sulfides in turn precipitate heavy metals into metal sulfides. The growth rate of SRB has been reported to be relatively slow [Postgate, 1979]. The factors that inhibited the growth of this microorganism included the presence of oxygen and excessive amount of heat. However, once they grew, they were very strong in withstanding the aquatic environment. The growth was indicated by the blackening of iron salt. The environmental conditions that were suitable for bacterial growth were [Postgate, 1979]:

- Temperature ranging between -5° C and 75° C;
- pH ranging between 5 and 9.5;
- No oxygen;
- Redox potentials between -150 and -200 mV.

3.1 Metabolism of the bacteria

Dissimilating sulfate reducing bacteria belong to the class of microorganisms that use sulfates (SO_4^{--}) as electron acceptors.

There were two groups of dissimilating sulfate reducing bacteria; Desulfovibrio and Desulfotonaculum. Desulfovibrio use lactate, pyruvate and ethanol as carbon and energy sources. Desulfotonaculum specialize in the oxidation of fatty acids, particularly acetates, while reducing sulfates to sulfides [Lappan, 1987].

The metabolic reactions of the Desulfovibrio group are:

$$2\ \text{Lactate} + SO_4^{--} \dashrightarrow 2\ \text{Acetate} + 2\ CO_2 + 2\ H_2O + S \quad (3.1)$$

$$4\ \text{Pyruvate} + SO_4^{--} \dashrightarrow 4\ \text{Acetate} + 4\ CO_2 + S \quad (3.2)$$

$$2\ \text{Ethanol} + SO_4^{--} \dashrightarrow 2\ \text{Acetic Acid} + 2\ H_2O + S \quad (3.3)$$

Desulfotonaculum's metabolic reaction was:

$$\text{Acetate} + SO_4^{--} \dashrightarrow H_2O + CO_2 + HCO_3 + S \quad (3.4)$$

Simultaneous relationship existed between the Desulfotonaculum and Desulfovibrio groups. Desulfovibrio will reduce sulfate to sulfide by producing acetate, while Desulfotonaculum utilize the acetate to convert the sulfate into sulfide.

To form cell membranes, enzymes, phospholipid and nucleic acids, the bacteria require both macronutrients and micronutrient. The list of essential nutrients is given in Table 3.1.

Table 3.1
The macronutrients and micronutrient required by the SRB (Sulfate Reducing Bacteria)

Macronutrients:	**Micronutrient:**
Phosphorous (P)	Zinc (Zn)
Potassium (K)	Copper (Cu)
Magnesium (Mg)	Cobalt (Co)
Calcium (Ca)	Manganese (Mn)
Sodium (Na)	Molybdenum (Mo)
Iron (Fe)	

3.2 Metals and SRB

The SRB are very tolerant in withstanding changes in the aquatic environment. They have a high survival capacity, even in the presence of high metal concentrations. They reduce the toxicities of metals by precipitating them as metal sulfides [Lawrence et al., WPCF, 37, 3]. High concentrations of dissolved H_2S, an intrinsic toxin to all living systems, inhibit or even stop growth unless metal ions are present for sulfide precipitation. Thus, sulfides control the toxicity of metals, while the metal ions prevent the danger of high concentrations of dissolved H_2S. This mutual need between the metal ions and sulfides to reduce the toxicity to the SRB allow the bacteria to continue to grow.

IV. EXPERIMENTATION

4.0 Experimental Set Up

In all, eight separate pyrex glass reactors were used in parallel, as shown in Figure 4.1. Each reactor was a three neck flask with a total volume of 500 mL. It was filled with plastic pall rings as packing material. Table 4.1 shows the void volume and porosity of the reactor. There were two separate feeding lines to each reactor, and only one effluent line. The two feeding lines were used to feed substrate and metal solution. The effluent line delivered the treated water to the effluent collector. The reactors were air tight by using the rubber stoppers to close the neck openings. The feed glass tubings were inserted to the bottom of the reactor to make it as an upflow system.

Table 4.1
Reactor and Packing Volume

Total Volume	500 mL
Number of Rings	90
Packing Volume	50 mL
Void Volume	450 mL
Porosity, ϵ	0.9

The variable speed pump, which delivered substrate, was calibrated for a flowrate of 0.625 mL/min which provided the reactor with a HRT of 12 hours. Calibration of the pumping system was conducted by measuring the time required for the collection of

5 mL of effluent in a 10 mL graduated cylinder.

During the metal loading study, both the substrate and metal lines were activated. The variable speed pump, which delivered substrate, was calibrated for a flowrate of 0.536 mL/min. Meanwhile, the pump that delivered metal was calibrated for a flowrate of 0.0893 mL/min. The two flowrates together provided a 12 hours HRT for the system. Both lines were calibrated separately.

The temperature of the system was maintained at approximately 20 degrees Celsius. All reactors were immersed in the water bath to maintain a constant temperature. The substrate was mixed continuously using a magnetic stirrer to keep a homogeneous solution.

The effluent collector system consisted of an effluent inlet, air vent, sample outlet, and effluent outlet. The purpose of the air vent was to make sure that there was no gas accumulation in the effluent collector. The gas produced by the anaerobic process (H_2S) was considered toxic in high concentration. It also had an unpleasant odour. Therefore, good ventilation was required for a sound operation. The sample outlet was used for collecting the sample for analysis. The effluent outlet was connected to the drain.

The entire apparatus was made either from plastic or glass to prevent corrosion, which could be caused by the presence of hydrogen sulfides. Figure 4.1 displayed a complete illustration of the whole system.

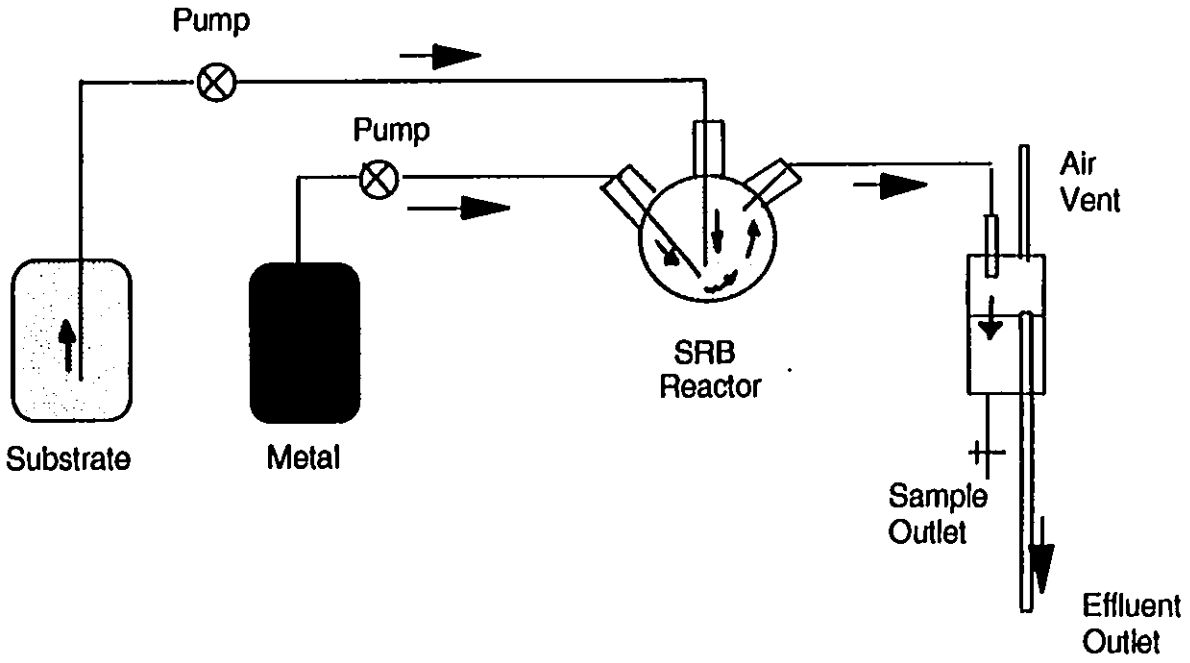


Figure 4.1
Upflow Anaerobic Fixed Film Reactor and Supporting Apparatus

4.1 Operational Parameters

There are several operational parameters that affect the performance of biological anaerobic filters, seeded with sulfate reducing bacteria (SRB). These include hydraulic retention time (HRT), contact surface area and type of flow, temperature, pH, and redox potential [DeWalle et al., 1979; Maree et al., 1985]. The total metal removal efficiencies depend on HRT, while temperature, pH, and redox potential regulate the bacterial growth and performance.

4.1.1 Hydraulic Retention Time

Hydraulic retention time (HRT) is the time required for a particle to pass through the entire reactor. Therefore, it indicates the contact time between the wastewater and the biomass. The contact time affects the mass transfer and metabolic kinetic of the biomass. As a result, it influences the sulfide production. The decrease in retention time would decrease the sulfide production [Lappan, 1987]. Furthermore, the total heavy metal removals are also time dependent. It has been shown that the decrease in HRT would decrease the total heavy metal removal efficiencies, due to the increase in the suspended solids and associated metals in the effluent. However, the increase in HRT would prolong the time taken to treat the wastewater and increase the cost. Thus, the designed HRT should maintain a good filter performance and be economically feasible. Lappan (1987) found that 12 hrs HRT was able to maintain a good bacterial performance and heavy metal separation. Maree and

Strydom (1985) indicated that at 6 hrs HRT, the sulfate reduction was too slow. They concluded that 11 hrs was considered to be the optimum for sulfate reduction. Others have used a higher HRT. This study employed a hydraulic retention time of 12 hours.

4.1.2 Contact Surface Area and Flow Type

The surface area represents the area available for the bacteria to adhere and to be exposed to their substrate. In this study, packing material was used to increase the surface area. The purpose of increasing the surface area was to retain more biomass, while maintaining sufficient contact between the biomass and the wastewater.

Generally, there are two types of flows in filters, upflow and downflow. Upflow reactor was employed in this study. Its hydraulic regime was a Plugflow as shown in Appendix II. In a plugflow model, all particles entering the reactor stay in the reactor for the same amount of time. The mixing of the reactor was obtained by the upflow of the wastewater.

4.1.3 Temperature, pH and Redox Potential

Temperature, pH and redox potential are considered to be important parameters for the bacterial growth. Mesophilic bacteria have an optimum growth temperature at 37 degrees Celsius, whereas for Thermophilic bacteria, it is 67 degrees Celsius. The extreme temperatures for SRB to survive have been reported to be -5 and 75 degrees Celsius [Postgate, 1979]. In this research, the temperature

was maintained at room temperature, at approximately 20 degrees Celsius.

The optimum pH for bacterial growth generally ranges between 6.5 and 7.5. However, according to Postgate (1979), SRB have been able to survive at pH between 5 and 9.5. The pH in this study was maintained between 6.5 and 8 depending on the nature of the feed.

Redox potential indicates the electron activity of the bacterial environment. An initial value of redox potential below -100 mV is desirable for the initiation of SRB growth [Postgate, 1979]. Hydrogen sulfide, the product of sulfate reduction, can maintain redox potential at -100 mV or less.

4.2 Experimental Phases

The main objective of this study was to remove heavy metals from the wastewater using SRB in the upflow anaerobic fixed film reactor (UAFFR) and to establish its maximum heavy metal loadings.

Sulfides were the precipitants that were used to precipitate heavy metals. They were the product of SRB's respiratory oxidation of organic compounds. Thus, maximizing their production was essential in order to maximize the filter performance. The preliminary studies were carried out to examine the following factors that affected the sulfides production:

- organic loading
- phosphate requirement

4.2.1 Bacterial Seeding

In all, eight upflow anaerobic fixed film reactors were used. Six of them were seeded with anaerobic sludge taken from a SRB reactor previously used by Lappan (1987). The other two were treated as controls and were not seeded with SRB. The seeding of reactors was done by pouring 10 mL of sludge to each reactor and then filling it with the diluted substrate. Table 4.2 shows the substrate composition used in this study. Tap water was used to make the substrate dilution.

Table 4.2
Substrate Composition Used in this Study

Compounds	**Concentration**
$MgSO_4.7H_2O$	1.3 g/L
NH_4Cl	0.43 g/L
Sodium Lactate	0.5 g/L

The bacteria in the reactor were fed with the substrate continuously based on 12 hours HRT. The temperature remained near 20 degrees Celsius and the pH was kept between 7-8. The blackening of the medium as a whole was an indication of the growth of SRB. The black particles were actually FeS precipitate. The sulfide, which was produced during bacterial reaction, reacted with iron to form iron sulfide (FeS).

4.2.2 Organic Loading

The sulfide production rate increased until the biofilm

thickness had fully developed for substrate diffusion. After that, further organic addition did not increase the sulfide production rate. In this phase, the study was focused on establishing the maximum sulfide production after which any further addition of organic did not reduce the sulfate significantly. Lactate was used as the organic source. The relationship between lactate loading and sulfide production was derived.

There were four sets of reactors. Each set consisted of two reactors, as shown in Table 4.3. Reactor IA and IB contained no SRB and acted as controls. All reactors were fed with substrate (Table 4.2) continuously. Ammonium chloride, the nitrogen source, was added to the substrate. However, other nutrient requirements, such as phosphorus, were derived from tap water.

Initially all reactors were fed sodium lactate at a concentration of 0.5 g/L. After sulfide production reached the steady state, the amount of sodium lactate was increased to the next level, as shown in Table 4.3, until further addition would not increase the sulfide production significantly.

Table 4.3
Sodium Lactate Loading - Without Phosphate

	Bacteria	Sodium Lactate Level, g/L
Reactor IA, IB	No	0.5, 1, 1.5, 2, 3
Reactor IIA, IIB	Yes	0.5, 1, 1.5, 2, 3
Reactor IIIA, IIIB	Yes	0.5, 1, 1.5, 2, 3,4
Reactor IVA, IVB	Yes	0.5, 1, 1.5, 2, 3,5

Parameters measured were sulfide, sulfate, temperature, pH and flowrate. Flowrate was measured to confirm the desired 12 hours HRT. HRT was calculated by dividing void volume with the flowrate. Bacterial count was made at the end of the study to determine the number of active bacteria.

4.2.3 Phosphate Addition

It was assumed, as in the above study, that nutrient requirement would be met by the tap water used for substrate dilution. However, Kelly and Switzenbaum found better bacterial performances in the nutrient-supplied experiments than nutrient-limited experiments. Therefore, The effect of nutrient addition, phosphorus in particular, to the anaerobic filter, was studied.

The experiments were carried out by adding Phosphates to the substrate solution. KH_2PO_4 and K_2HPO_4 were the phosphate sources. Postgate (1979) added 0.35 g/L PO_4 in his "Medium B", while Wijaya (1991) added 0.18 g/L PO_4 to the substrate in their studies.

Initially, 0.35 g/L phosphate was added to the system. Then it was decreased to 0.18 g/L. The results were compared to determine the amount of phosphate needed for optimum filter performances. Table 4.2 shows the substrate composition, before adding the phosphate. However, the sodium lactate concentration of 0.5 g/L was changed to 1 g/L in this phase.

After determining the amount of phosphate needed to have satisfactory filter performance, the filters were subjected to a similar condition to the one in the organic loading study. The

filters were fed with different lactate loadings (Table 4.4) until a maximum sulfide production was achieved. Then, the results were compared with the previous study.

Table 4.4
Sodium Lactate Loading - Phosphate Addition

	Bacteria	Sodium Lactate Level, g/L
Reactor IA	No	1, 1.5, 2, 3
Reactor IIB	Yes	1, 1.5, 2, 3
Reactor IIIA, IIIB	Yes	1, 1.5, 2, 3, 4
Reactor IVA, IVB	Yes	1, 1.5, 2, 3, 5

At this stage, reactors IB and IIA were dropped to avoid repetitive work. It was decided that one non-bacterial and one bacterial control was enough to have presentable results. Parameters monitored were sulfide, sulfate, flowrate, pH, temperature, bacteria count, and total organic carbon (TOC). TOC was used as a measure of organic content. Bacterial count was made at the end of the study.

4.2.4. Heavy Metal Loading Rates

The heavy metal removal efficiencies were investigated under different metal loading rates. The purpose of this investigation was to determine the maximum metal loadings that could be precipitated with the sulfide produced by the SRB. The heavy metals tested were lead (Pb), copper (Cu), chromium (Cr), cadmium (Cd).

Synthetic metal solutions were fed to the reactors. The metal solutions were prepared by dissolving respective metal sulfates in concentrated HNO_3 and then diluting with tap water

Six reactors were used under different operating conditions to study the metal loadings. They were:

- Reactor IA : Control; without bacteria; Pb, Cr, Cu, Cd
  Used to monitor the heavy metal precipitation in the absence of SRB.
- Reactor IIB : Control; with bacteria; no metals
  Used to determine the ability of SRB to produce sulfides in the absence of heavy metals.
- Reactor IIIA: Bacteria; Lead
  Used to determine lead removal under different lead loading rates.
- Reactor IIIB: Bacteria; Chromium
  Used to determine chromium removal under different chromium loading rates.
- Reactor IVA : Bacteria; Copper
  Used to determine copper removal under different copper loading rates.
- Reactor IVB : Bacteria; Cadmium
  Used to determine cadmium removal under different cadmium loading rates.

As explained before, the heavy metal and substrate were fed separately. The heavy metal and substrate flowrates are shown in Table 4.5. The heavy metal flowrate was lower than the substrate

flowrate. The purpose of using lower flowrate for the heavy metal feeding was to neutralize the acidic pH of the metal solution as soon as it entered the reactor to pH values between 6.5 to 7.5. Therefore, the inhibition of the SRB growth due to acidic pH was avoided.

Table 4.5
Heavy Metal and Substrate Flowrates

	Q
Heavy metal feeding	0.0893 ml/min
Substrate feeding	0.536 ml/min

Parameters monitored were residual sulfide, sulfate, flowrate, pH, redox potential, dissolved metal, and total metal. The purpose and significance of each parameter are listed below:

- Residual sulfide concentration indicated excess sulfide which was still available for dissolved metal precipitation.
- Sulfate was used to calculate the total sulfate reduced by SRB.
- Flowrate provided control on the HRT.
- pH readings provided information on pH of the metal solution, substrate, and effluent.
- Redox potential values were used to develop a relationship between the excess sulfide concentration and oxidation-reduction

potential of the effluent.

- Dissolved metal concentrations were used to calculate the dissolved metal removal efficiencies.
- Total metal concentrations were used to calculate the total metal removal efficiencies.

4.3 Method of Analysis

All analytical methods conformed to "Standard Method" (STDM, 1989). Table 4.6 lists the methods of analysis, testing frequency, and the sample size used. All samples were taken by collecting the needed aliquot in a beaker just before the test was to be performed.

4.3.1 Sulfide

The Iodometric method [STDM, 1989] was used to determine the sulfide concentration in the effluent. However, this method suffered interferences from reducing substances, such as thiosulfate, sulfite, and various organic compounds. In order to overcome this problem, the sample was pretreated using zinc acetate, as described in STDM 4500-S C (1989)

Total sulfides were measured in the organic loading and phosphate addition studies. However, in the metal loading study, some sulfides had precipitated as metal sulfides. Thus, residual sulfides were measured instead of total sulfides. For measuring the

Table 4.6
Methods of Analysis Used in this Study

Parameter	Method of Analysis*	Organic Loading		Phosphate Addition		Metal Loading	
		Sample Volume	Frequency of Testing Perweek	Sample Volume	Frequency of Testing Perweek	Sample Volume	Frequency of Teating Perweek
Sulfide	4500-S B,C,E	10 mL	2	10 mL	2	10 mL	2
Sulfate	4500-SO4 E	5 mL	2	5 mL	2	5 mL	2
pH	Electrode	A	2	A	2	A	2
TOC	5310 C	-	-	250 uL	1	-	-
ORP	Electrode	-	-	A	2	A	2
Bacterial Count	Rapid Check II	A	-	-	-	B	-
Flowrate		A	2	A	2	A	2
Metal (Dissolved and Total) 3120 A,B							
Lead	DC Plasma	-	-	-	-	A	2
Chromium	DC Plasma	-	-	-	-	A	2
Cadmium	DC Plasma	-	-	-	-	A	2
Copper	DC Plasma	-	-	-	-	A	2

A-Analyzed
B-Depending on the sample dilution
* Method Number in the Standard Method (1989)

residual sulfides, the insoluble matter in the sample was removed with aluminum hydroxide floc that was settled, leaving a clear supernatant for analysis. The procedures is described in STDM 4500-S B (1989).

4.3.2 Sulfate

Sulfates were analyzed by Turbidimetric method described by STDM 4500-SO4 E (1989). Barium chloride ($BaCl_2$) was added to the sample to form $BaSO_4$ crystals of uniform size. A nephelometer measured the light absorbency of the $BaSO_4$ suspension and the reading was correlated with sulfate ion concentration from the standard curve (see Appendix I).

4.3.3 Bacterial Count

Bacterial count was done by using "Immunoassay Test Kit" for the detection of Sulfate Reducing Bacteria [Rapid Check II, Conoco]. It used purified antibodies to detect the enzyme adenosine-5'-phosphosulfate (APS) reductase which was common to all strains of SRB.

4.3.4 Total Organic Carbon (TOC)

The total organic carbon was used to measure the organic content. The method used persulfate to oxidize organic carbon to carbon dioxide in the presence of ultraviolet light. Dohrman DC-180 Carbon Analyzer was used to determine TOC. High and low standard solutions [Rosemount Analytical, 1989] were prepared to calibrate

the instrument, each time it was run. There were no pretreatments of the samples prior to the analysis.

Chemical oxygen demand (COD) and biological oxygen demand (BOD) are the other methods normally used to measure the organic content. However, COD and BOD include not only the organic but also the inorganic substances, such as sulfides, ferrous ions and nitrites. The inorganic substances would interfere with the results. Also, BOD requires a five day incubation period. The five day incubation period has been found to allow for the consumption of only 70 to 80 percent of the total organic [Lappan, 1987]. Therefore, TOC was the preferred method to determine the organic content of the samples.

4.3.5 Redox Potential

The platinum and calomel electrodes were used to measure ORP. A verification of the electrode response was conducted using a pH buffer solution saturated with quinhydrone [Petersen, 1966]. Refer to Appendix III for ORP calculation.

It was not possible to obtain stable measurements in fluids containing biological matter. The reason was that the redox system contained in the solution would only slowly exchange electrons with the platinum electrode [Petersen, 1966]. Lappan (1987) had found that the electrodes required over one hour to reach equilibrium. It was suggested that, to ensure consistency, all measurements should be taken after ten minutes, which would ensure an ORP measurement of at least 95% of the relative equilibrium response.

4.3.6 Heavy Metals

Directly Coupled Plasma (DCP) method [STDM, 1989] was utilized to measure dissolved and total metal concentrations. The metals analyzed were copper (Cu), cadmium (Cd), chromium (Cr), and Lead (Pb). The samples for the total metal analysis were first digested with nitric acid , as prescribed by STDM 3030 E (1989), whereas the samples for dissolved metal analysis were filtered with 0.45 um cellulose acetate filter paper and then acidified. All samples were stored at 4° Celsius before being analyzed on a Beckman Spectraspan V Plasma Spectrophotometer [Spectrametric].

Each time the spectrophotometer was used, high and low standard solutions were prepared to calibrate the instrument. The low standard solution had a concentration of zero mg/L heavy metal. The high standard solution's concentration was prepared depending on the range of metal concentration in the sample. Thus, each run would produce different instrumental limit of detection (LLD). Appendix I provides the details for the calculation of LLD.

V RESULT AND DISCUSSION

5.0 General

Organic loading study was focused on the relationship between sulfide production and organic loading rate. The phosphate addition study was conducted to study the significance of nutrient (phosphorus) to the bacterial activities. The results from these preliminary studies provided the optimum conditions for SRB operation to produce sulfides. These optimum conditions were applied in the metal loading studies, to establish the maximum heavy metal concentration that the filter could treat.

5.1 Organic Loading Rate

Eight reactors were fed with substrate continuously. These were operated as a plugflow-upflow system as shown in Appendix II. Ammonium chloride, the nitrogen source, was added to the substrate. All other nutrient requirements, such as phosphorus, were derived from the tap water.

Figure 5.1 to 5.4 show the sulfate loading rate and sulfide production rate versus time for Reactors I, II, III, and IV. Subscripts "i" and "e" represent influent and effluent sulfate loading rates. The difference between influent and effluent values gives the amount of sulfate reduced and it is indicated by subscript "i-e". The amount of sulfide produced is designated by subscript "s". The sulfide production is expressed as equivalent

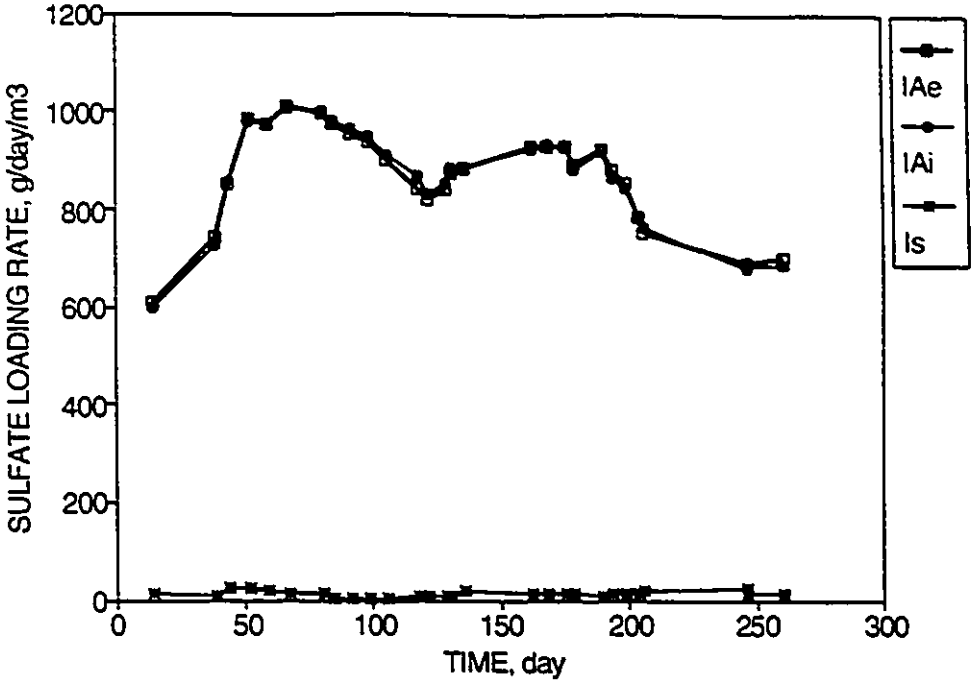
SO_4 for comparison purposes.

Figure 5.1 provides the results for Control Reactors IA and IB, which had no bacteria. The purpose of the control units were to demonstrate that the sulfate reduction occurred primarily due to bacterial reaction and not due to chemical reaction. This figure shows that there were neither sulfate reduction nor sulfide production in control units.

Figures 5.2 to 5.4 show the sulfate reduction by SRB. It is observed that not all of the sulfates were converted, which indicates that sulfates were not the limiting factor in sulfide production. The sulfates were reduced to sulfides, following the stoichiometric equation:

$$4H_2 + SO_4 \text{ ----> } 4H_2O + S \qquad (5.1)$$

All these figures show that the amounts of sulfates reduced ("i-e") were generally higher than the sulfides produced ("s"). Postgate (1979) has pointed out that in the reduction process, SRB generate intermediate compounds (sulphite, thiosulfate) before producing sulfide. Figure 5.5 illustrates the pathway for dissimilatory sulfate reduction [Postgate, 1979]. As a result of incomplete reduction, some of the sulfates would be reduced to intermediate reducing compounds, instead of sulfides. Thus, not all sulfates reduced were converted to sulfides and this resulted in the discrepancy in the values between sulfates reduced and sulfides produced.



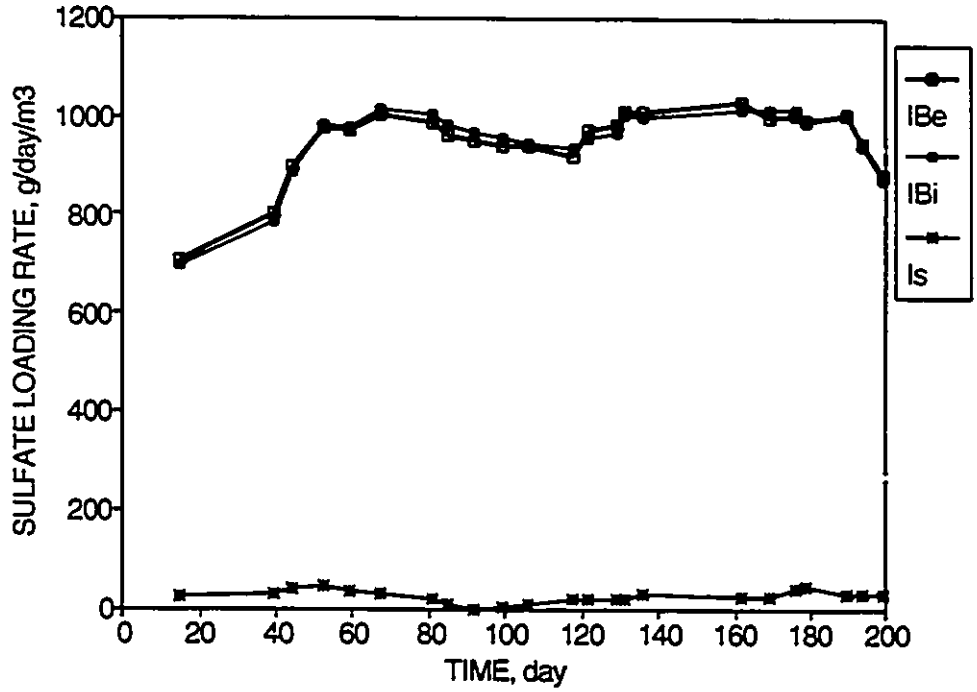
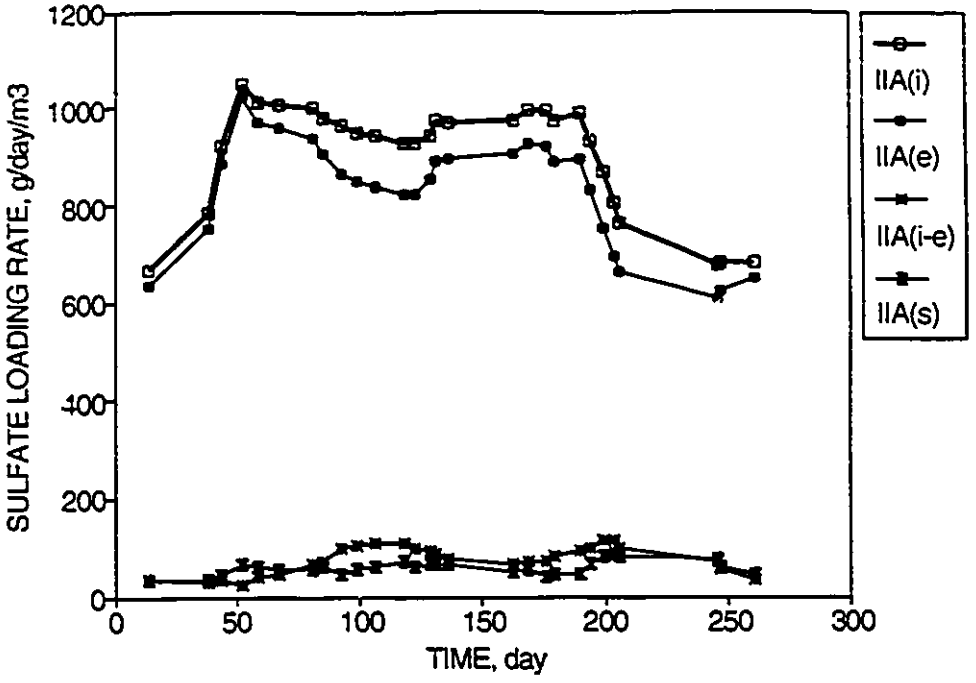


Figure 5.1
Influent and Effluent Sulfate Loading Rates and Sulfide Production Rate versus Time for Reactors IA & IB



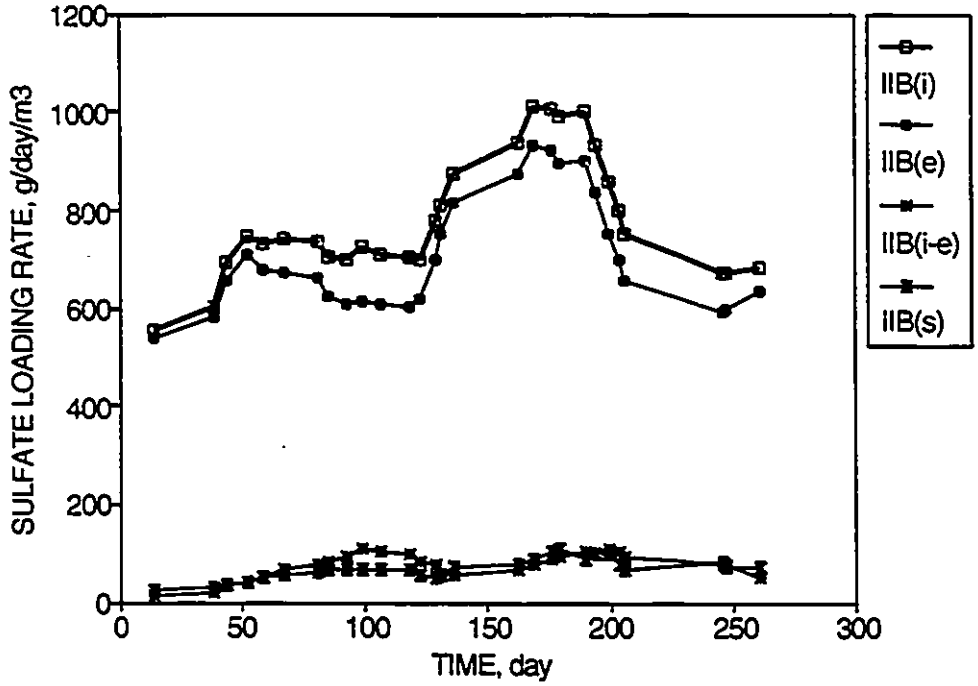
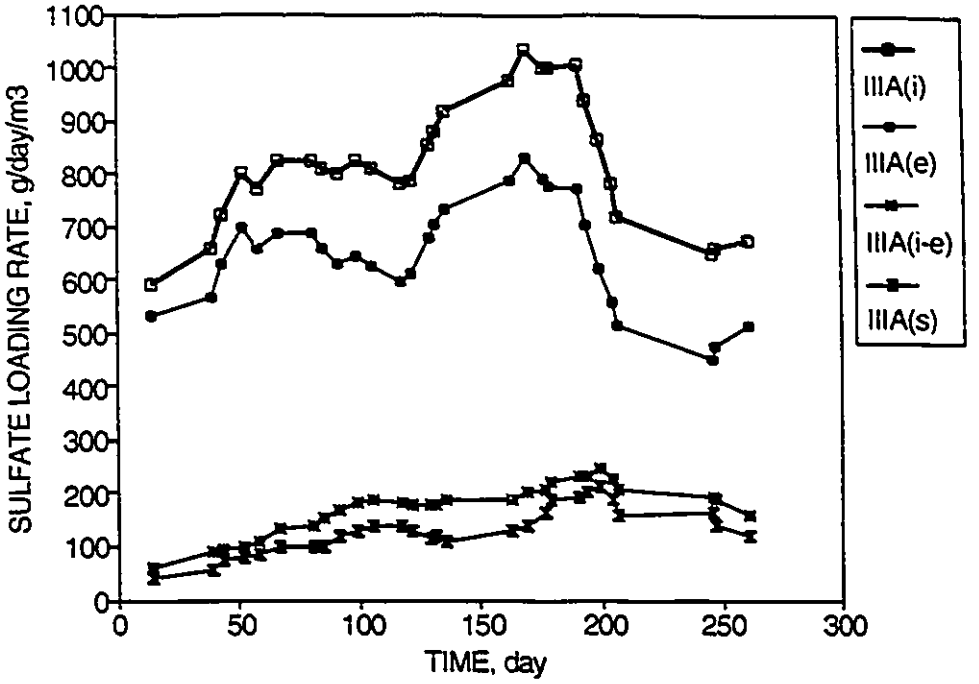


Figure 5.2
Influent and Effluent Sulfate Loading Rates and Sulfide Production Rate versus Time for Reactors IIA & IIB



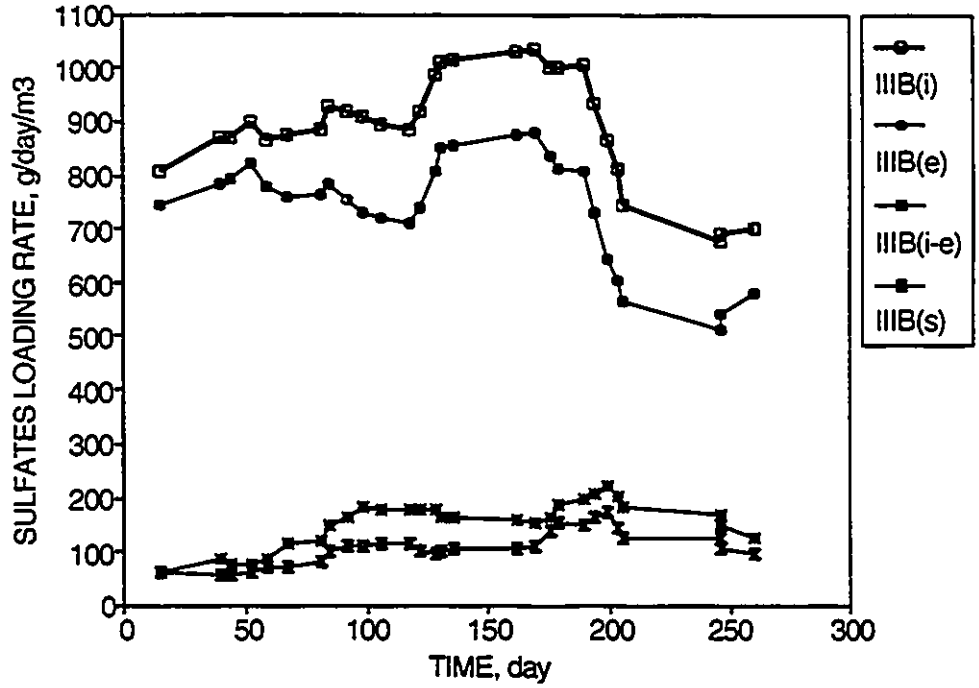


Figure 5.3
Influent and Effluent Sulfate Loading Rates and Sulfide Production Rate versus Time for Reactors IIIA & IIIB

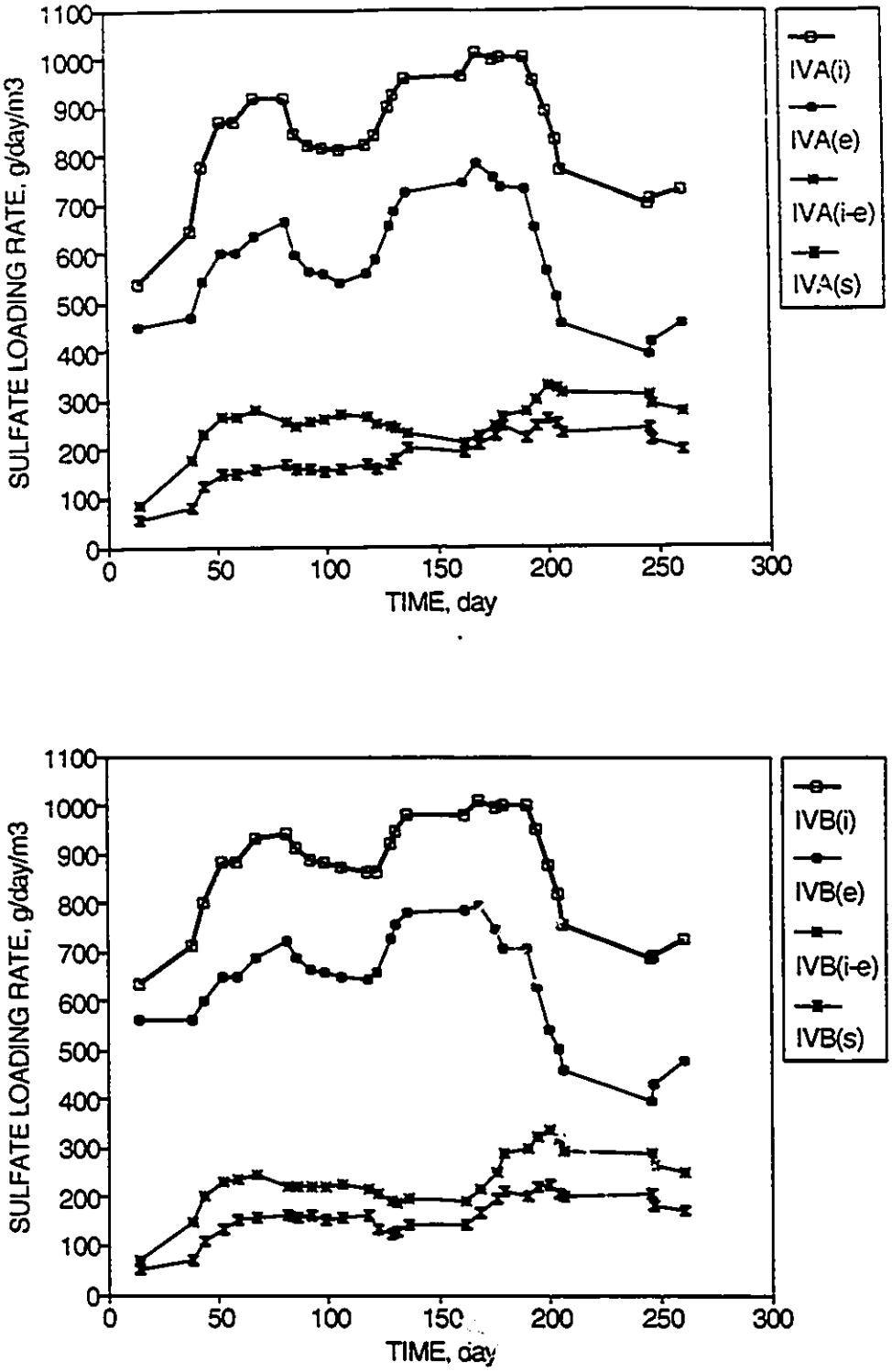


Figure 5.4
Influent and Effluent Sulfate Loading Rates and Sulfide Production Rate versus Time for Reactors IVA & IVB

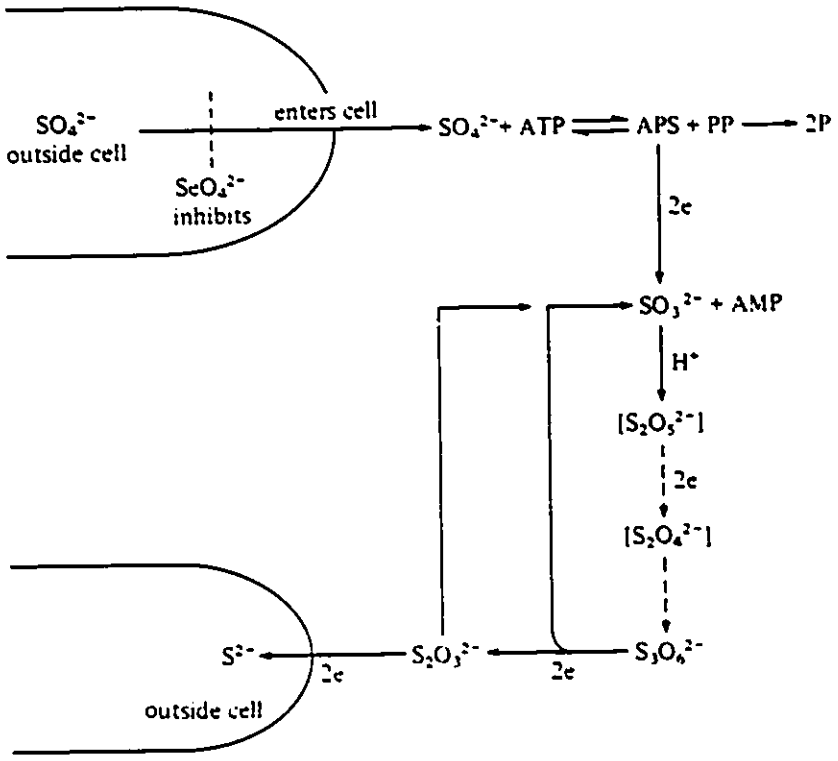


Figure 5.5
A Pathway for Dissimilatory Sulfate Reduction [Postgate, 1979]

Figure 5.6 shows the rate of sulfide production in Reactors IIA, IIB, IIIA, IIIB, IVA, and IVB. Each reactor behaved differently. As depicted on the graph, Reactor IV produced the most sulfides, while Reactor II produced the least amount. The difference in performance is attributed to the bacterial activity and density in the biofilm in each reactor. Table 5.1 shows the bacterial count in each reactor after 250 days. It is apparent that Reactors III and IV had higher bacteria count than Reactor II. Therefore, the higher the number of active bacteria, the more sulfate reduction occurred.

Table 5.1
Bacterial Count (cells/mL)- without PO_4 addition

Reactor	IIA	IIIA	IVA
Bacterial Count, cells/mL	10^4-10^5	10^6	10^6
Reactor	IIB	IIIB	IVB
Bacterial Count, cells/mL	10^3-10^4	10^5	10^7

The temperature of reactors was held constant at nearly 20° Celsius. The influent pH was maintained between 7.5 and 8. However, the effluent pH stayed around 7. The decrease of pH to neutral pH signifies the ability of the filter to neutralize the influent. The influent and effluent pH values versus time for Reactor II,

III, and IV are plotted in Figures 5.7 to 5.9.

The organic loading rate was studied in terms of lactate loading. The variations in lactate loading rate and sulfide production rate versus time are shown in Figures 5.10 to 5.12. The lactate loading rate was calculated as below:

$$R_L = Q * C_L / V \qquad (5.3)$$

R_L = lactate loading rate, M/T/L3

Q = feed flowrate, L3/T

C_L = lactate concentration in feed solution, M/L3

V = void volume of the reactor, L3

M, L, T represented mass, length, and time units respectively. The void volume in 500 mL reactor was equal to 450 mL.

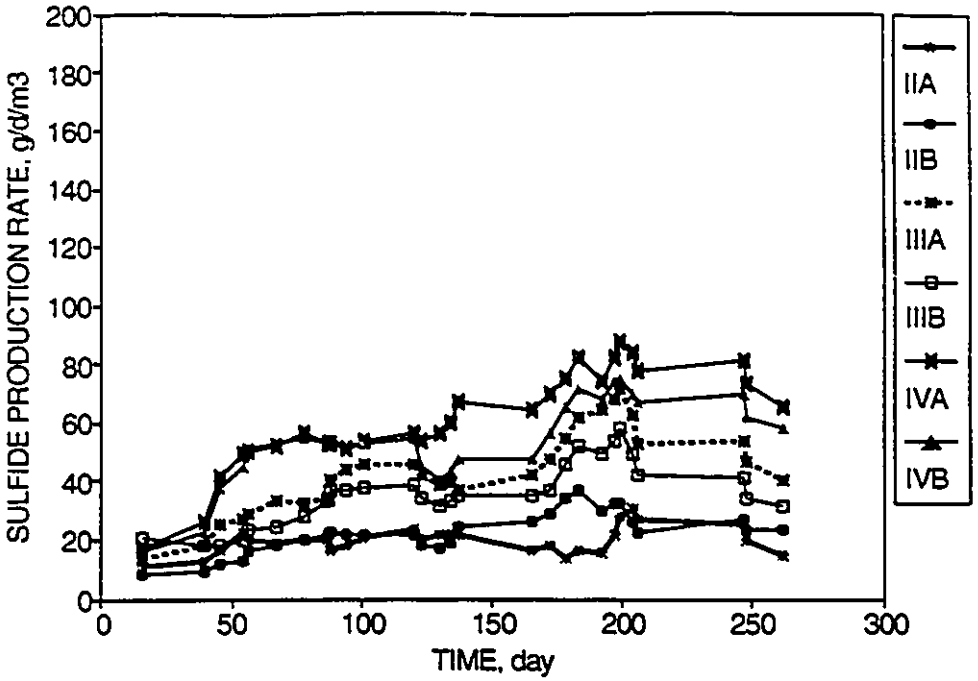


Figure 5.6
The Rate of Sulfide Production versus Time

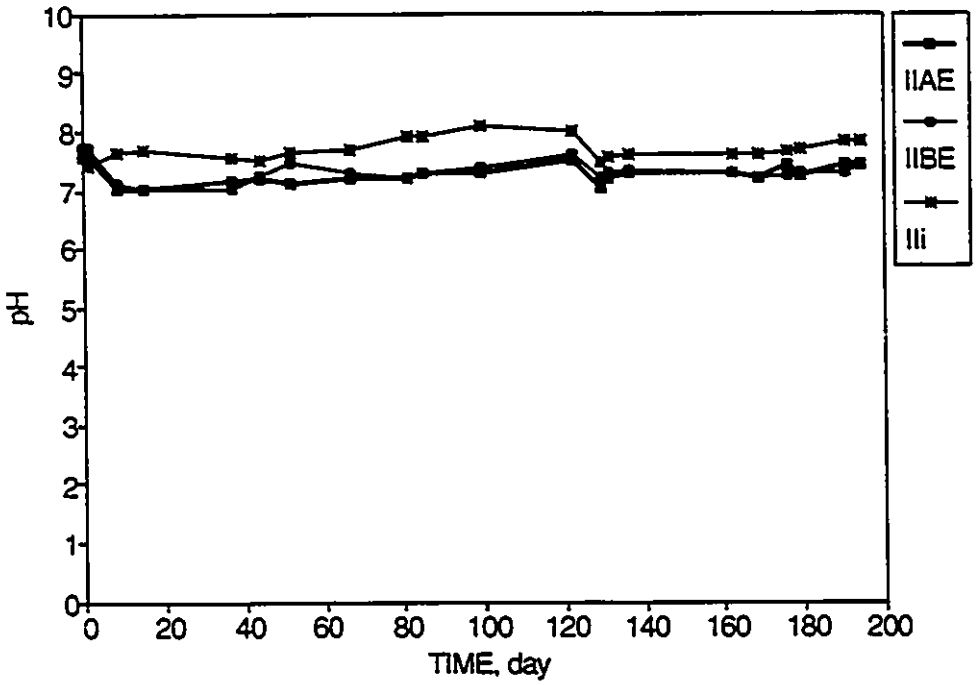


Figure 5.7
Influent and Effluent pH Values versus Time for Reactors IIA & IIB

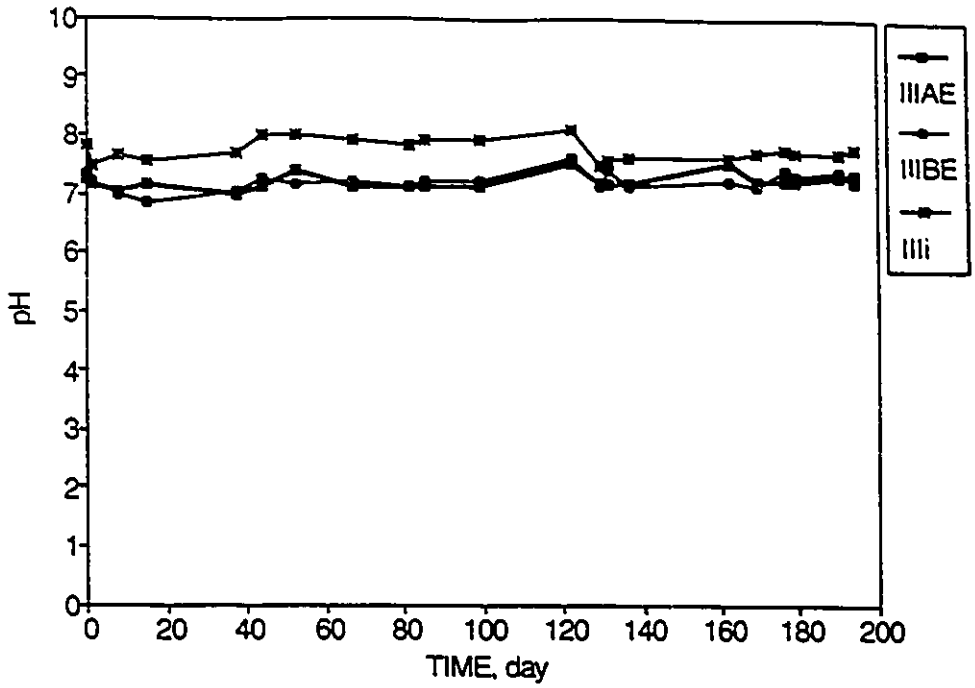


Figure 5.8
Influent and Effluent pH Values versus Time for Reactors IIIA & IIIB

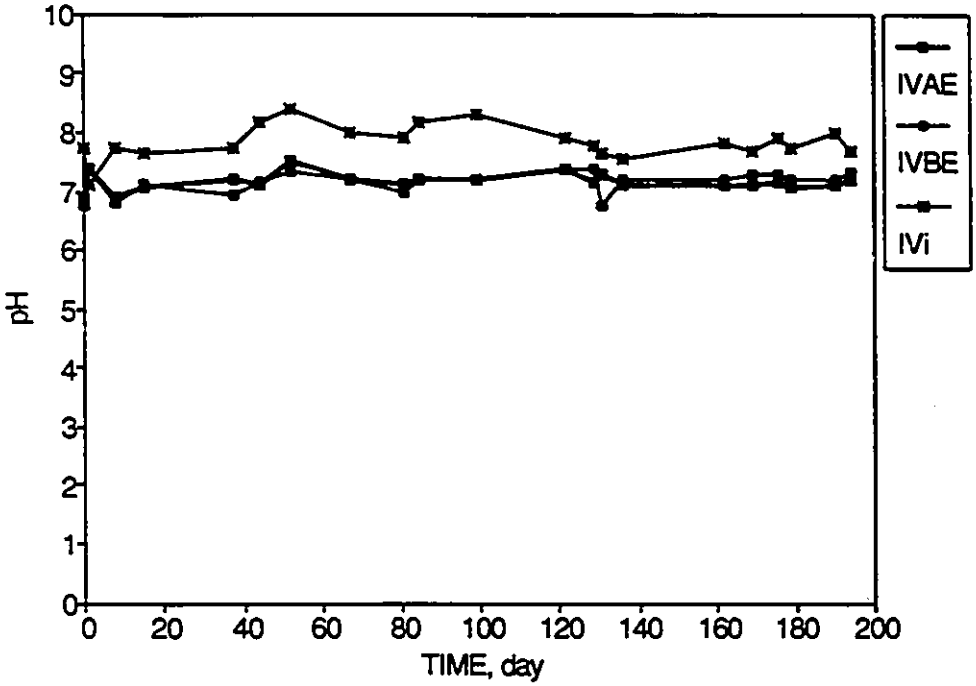


Figure 5.9
Influent and Effluent pH Values versus Time for Reactors IVA & IVB

Sodium lactate was used as a source of energy and carbon for bacterial activity. As reported before, each reactor behaved differently even when operated under similar conditions. Figures 5.10 to 5.12 show that under the same lactate loading, Reactor IV had the highest sulfide production, followed by Reactors II and III. However, all reactors followed the same pattern of sulfide production and lactate loading relationship. The sulfide production rate increased with the increase in lactate loading rate.

The relationship between sulfide production rate and lactate loading rate is plotted in Figure 5.13. The sulfide production rate increased with the increase in lactate loading rate. As the loading rate reached 2 kg/d/m3, the curve started to flatten. Beyond that point, the increase in lactate loading rate did not significantly contribute to additional sulfide production. According to Nielsen and Jacobsen (1988), the sulfide production rate in the biofilm increased so long as the biofilm was fully penetrated with organic and sulfate. The best fit (least squares) curve follows Equation 5.4 with R-squared = 0.582.

$$R_s = 18.58\ R_L^{0.641} \qquad (5.4)$$

R_S = sulfide production rate, g/d/m3

R_L = lactate loading rate, kg/d/m3

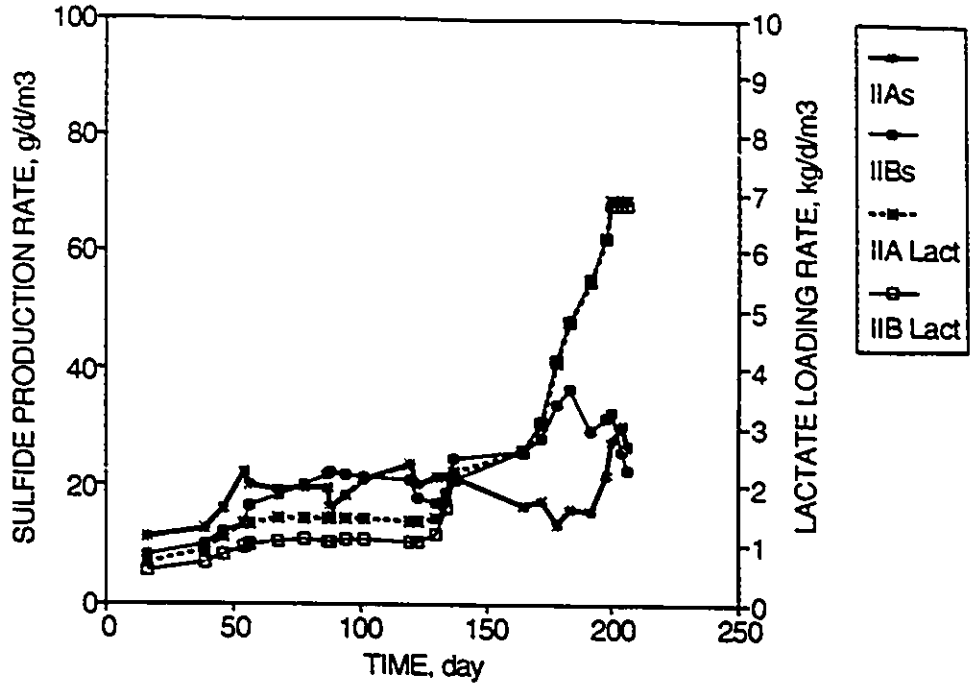


Figure 5.10
Sulfide Production and Lactate Loading Rates versus Time for Reactors IIA & IIB

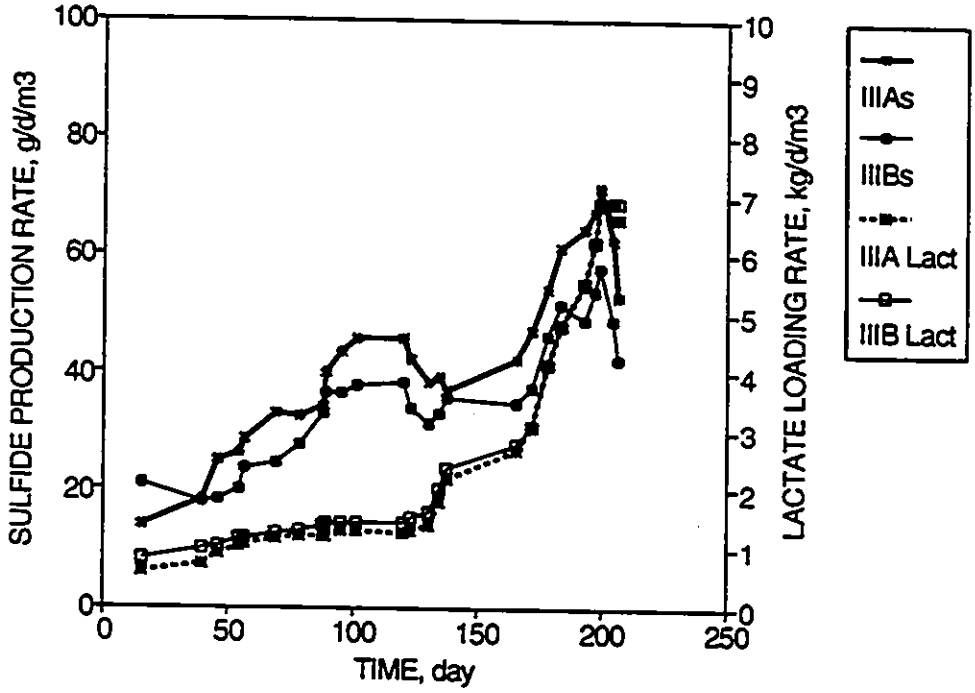


Figure 5.11
Sulfide Production and Lactate Loading Rates versus Time for Reactors IIIA & IIIB

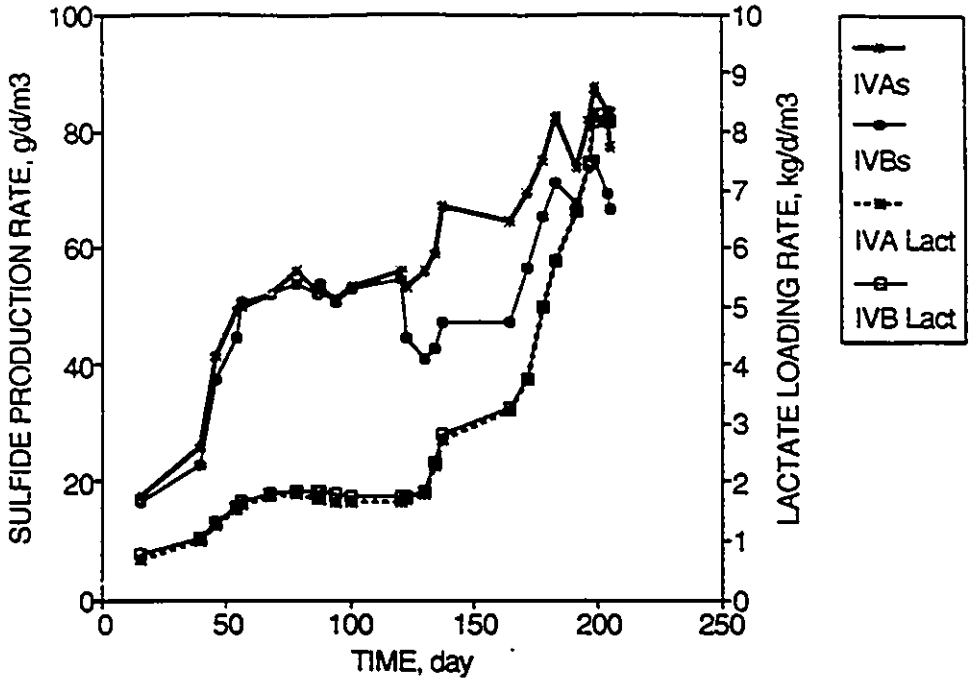


Figure 5.12
Sulfide Production and Lactate Loading Rates versus Time for Reactors IVA & IVB

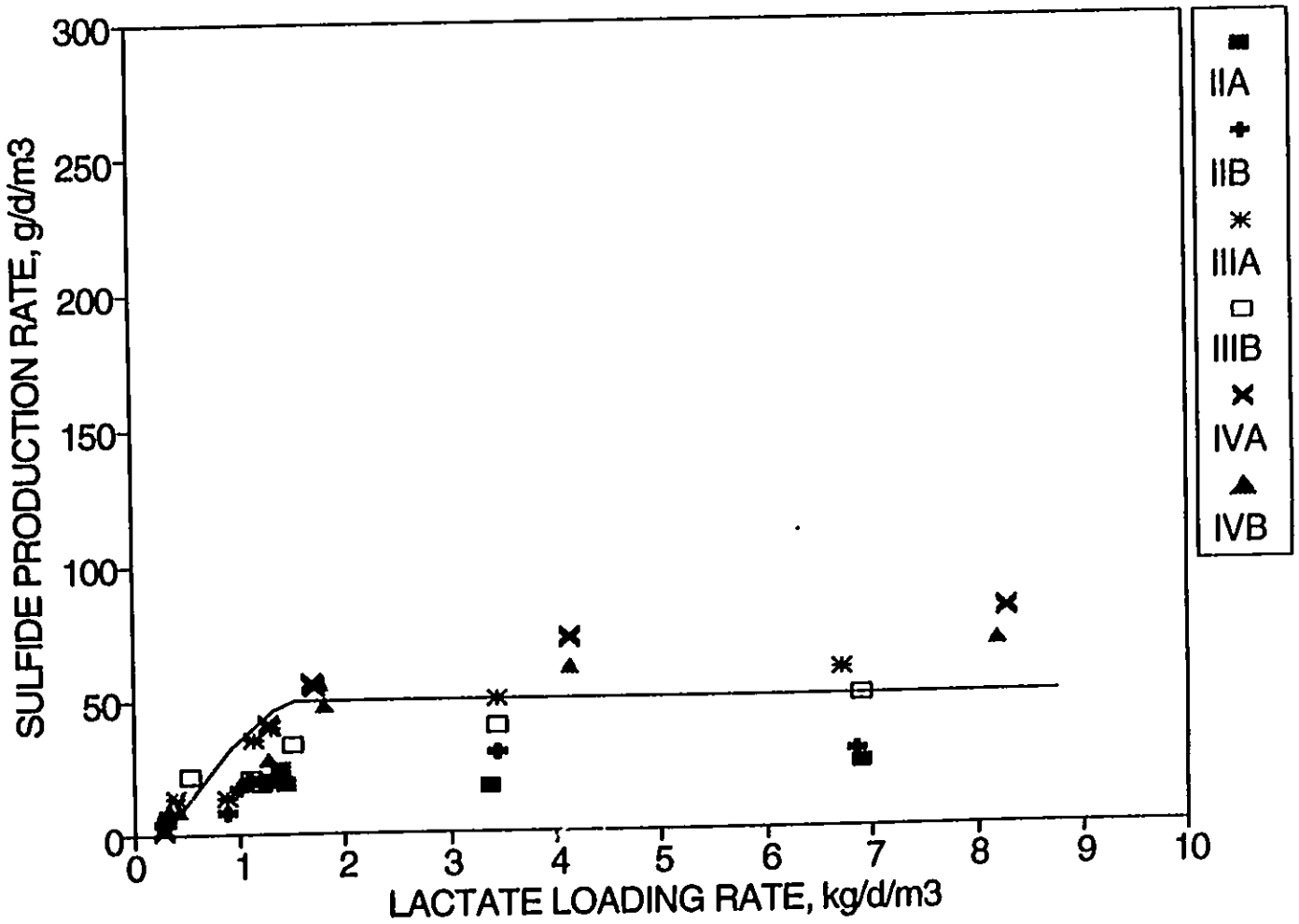


Figure 5.13
Sulfide Production Rate versus Lactate Loading Rate

Figure 5.13 shows that a certain minimum concentration of organic matter is required before sulfide is produced. This minimum organic concentration was necessary to deplete dissolved oxygen in the incoming influent. The oxygen depletion was essential for significant sulfide production in the biofilm [Nielsen et al., 1988].

5.2 Phosphate Addition

For this part of the study, phosphate was added to the substrate as a phosphorus source. Postgate (1979) recommended 0.35 g/L PO_4 in "medium B". In an unpublished previous work (Wijaya, 1990), 0.18 g/L PO_4 was used. Figure 5.14 shows the sulfide production rate under phosphate addition ranging between 0.18 g/L and 0.35 g/L. It is observed that the sulfide production rate with 0.35 g/L of PO_4 is the same as with 0.18 g/L of PO_4. Therefore, 0.18 g/L PO_4 was added to all subsequent studies on organic loading.

Figure 5.15 shows that there was no sulfate reduction in the Control Reactor IA. Figures 5.16 to 5.18 when compared to Figures 5.2 to 5.4 show that, after phosphate addition, the bacteria started to reduce more sulfate. Almost all sulfates were used up so long as the sulfate loading rate remained below 700 g/d/m3. It was necessary to keep the sulfate loading rate above this value so that it did not become the limiting factor in the reduction process. The influent sulfate content has little effect on the sulfate consumed as long as the sulfate loading rate is maintained

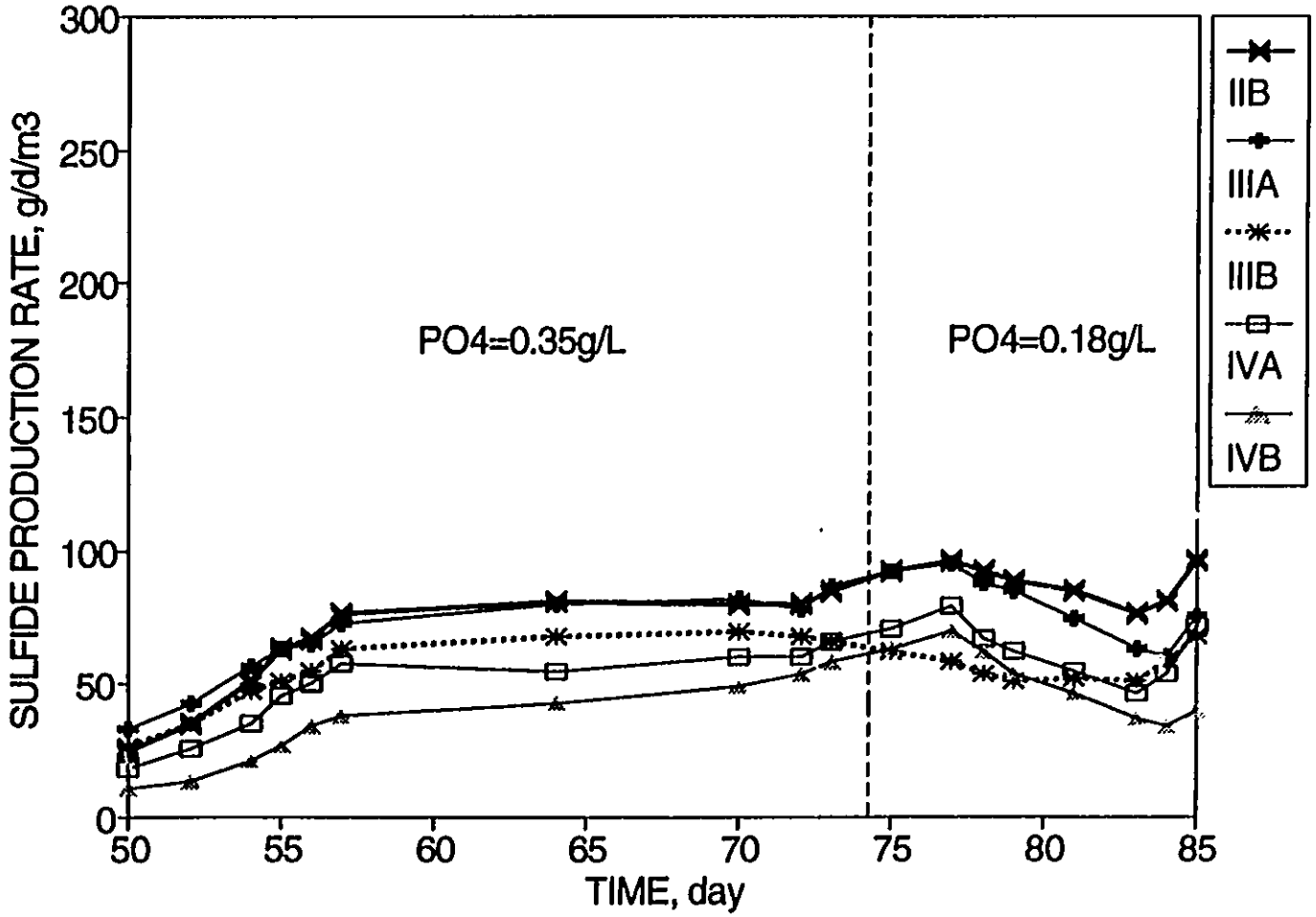


Figure 5.14
The Rate of Sulfide Production versus Time under Different Supplement Phosphate Concentrations

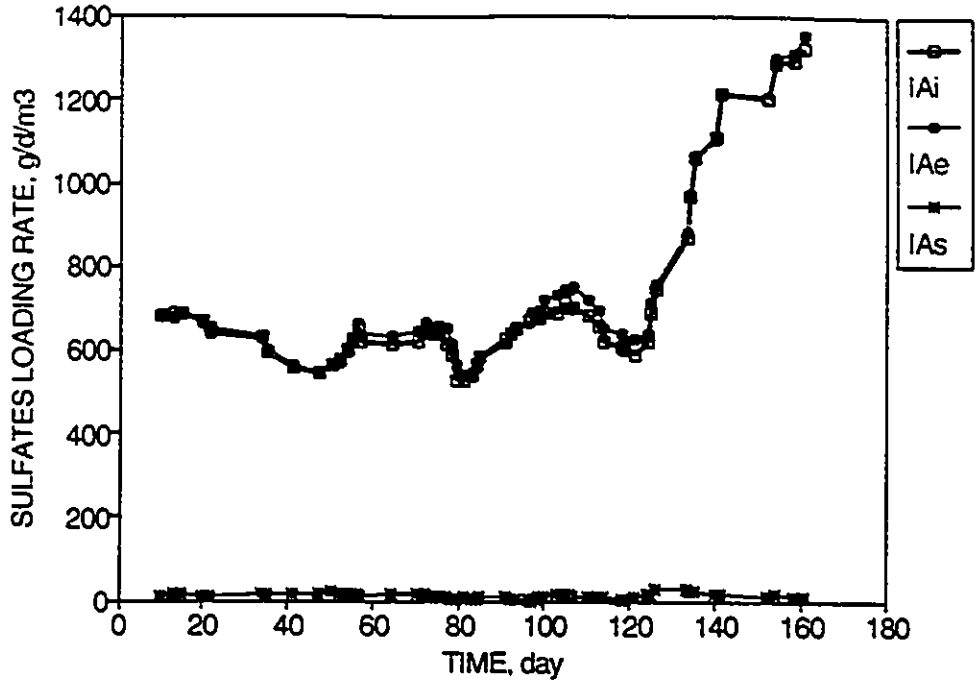


Figure 5.15
Influent and Effluent Sulfate Loading Rates and Sulfide Production Rate versus Time for Reactor IA - with PO_4 addition

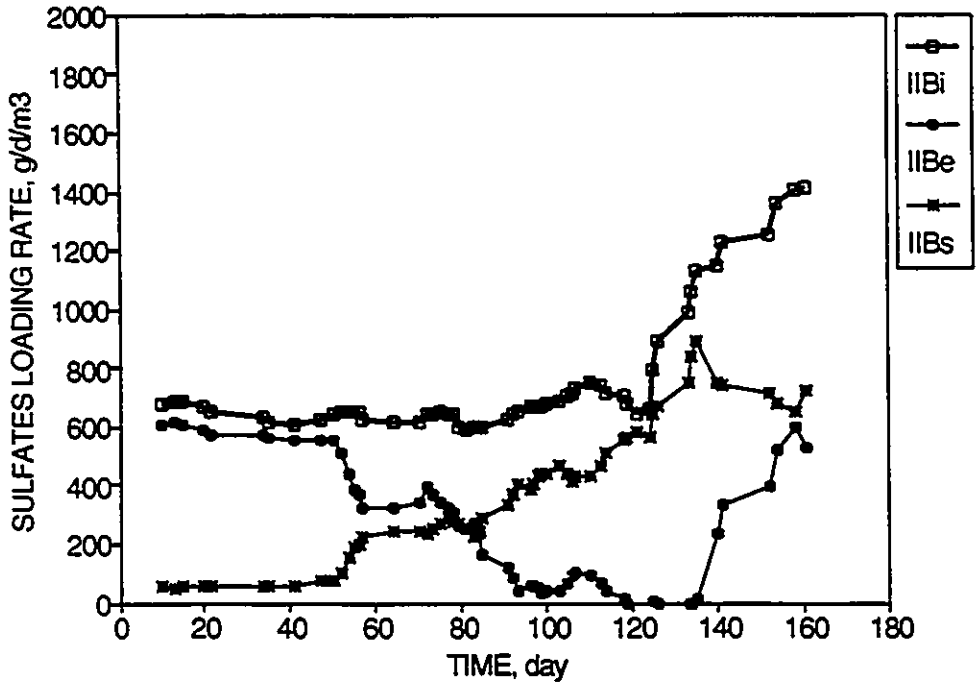
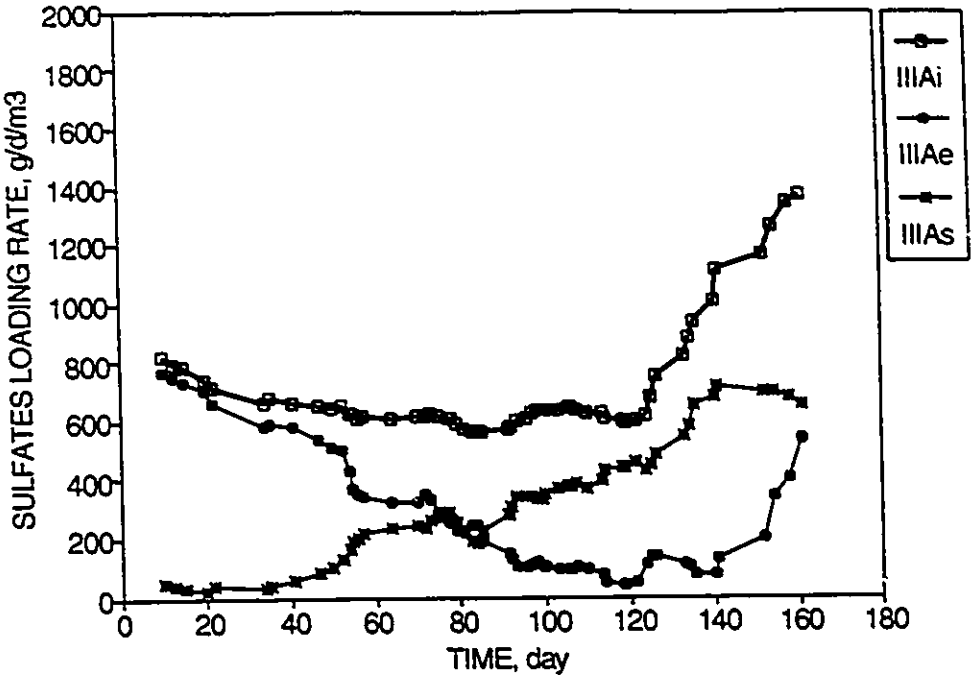


Figure 5.16
Influent and Effluent Sulfate Loading Rates, and Sulfide Production Rate versus Time for Reactor IIB - with PO_4 addition



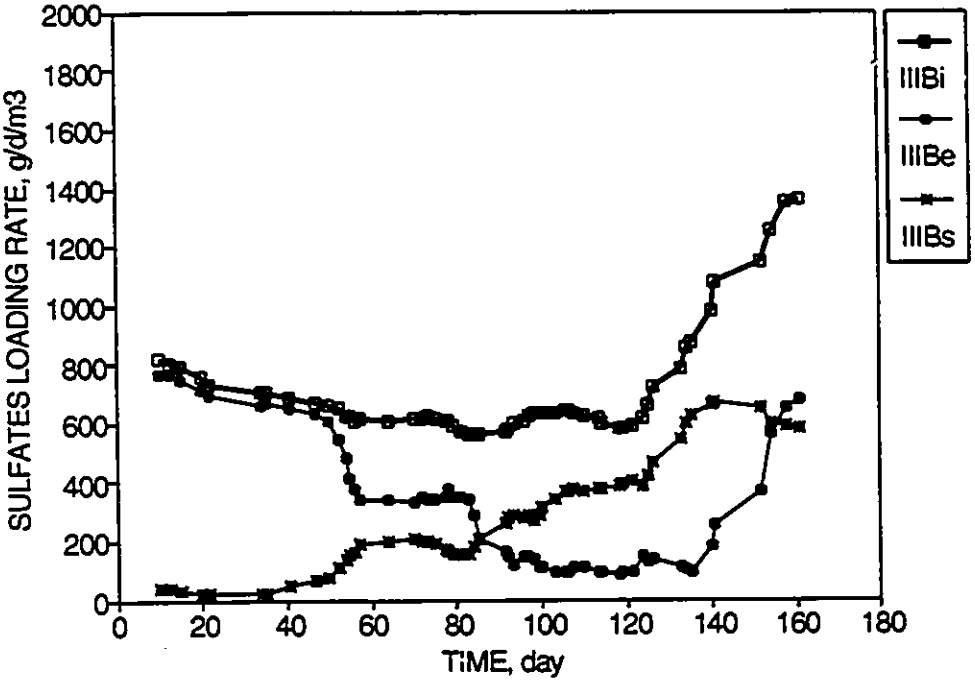
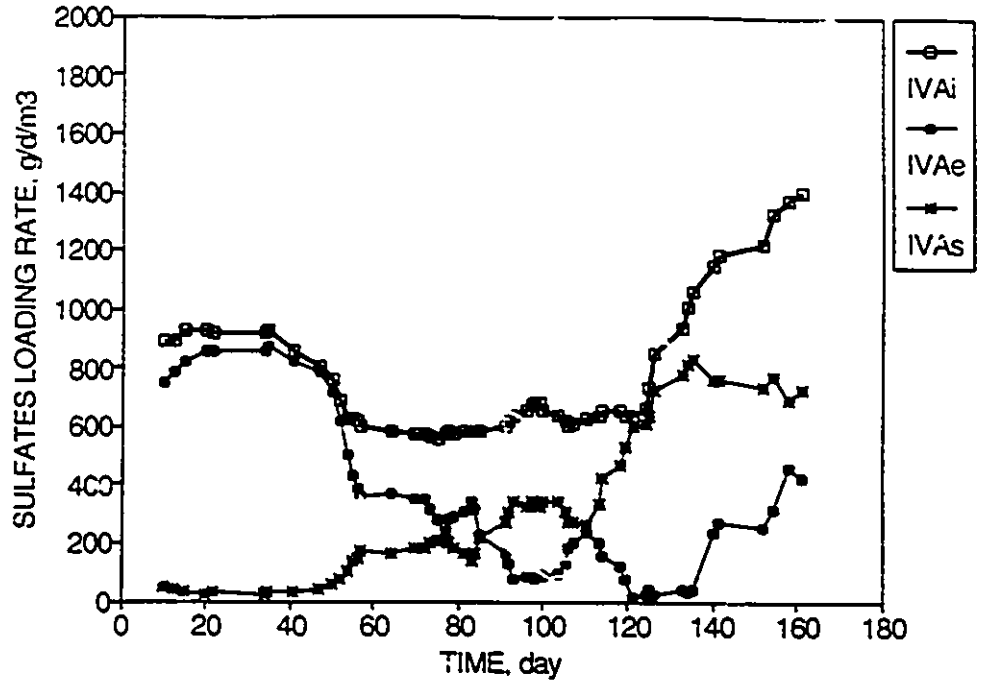


Figure 5.17
Influent and Effluent Sulfate Loading Rates, and Sulfide Production Rate versus Time for Reactors IIIA & IIIB - with PO_4 addition



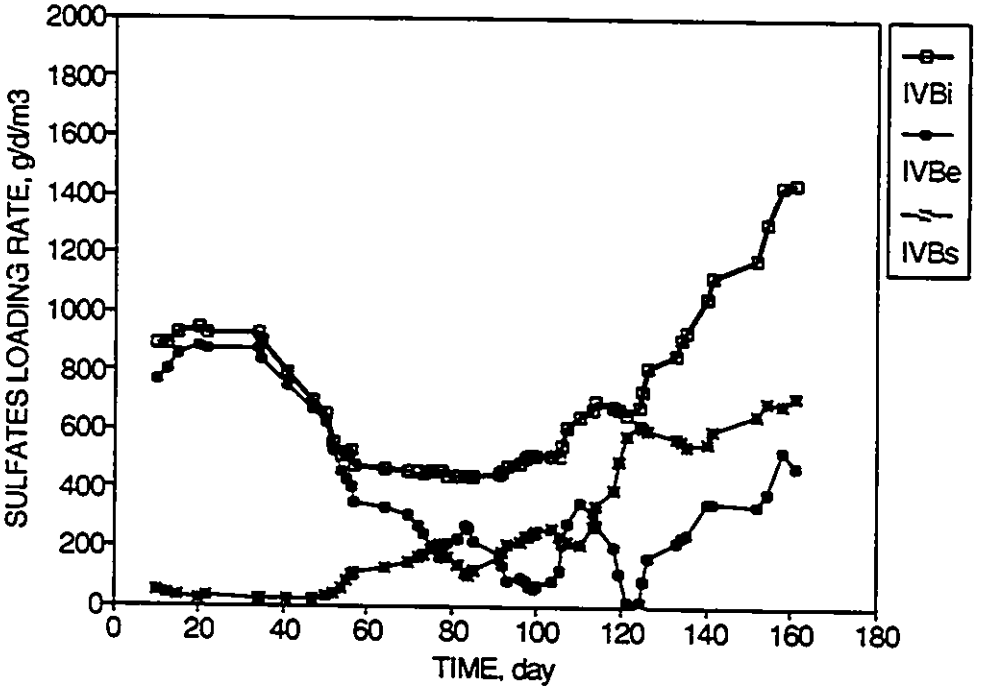


Figure 5.18
Influent and Effluent Sulfate Loading Rates, and Sulfide Production Rate versus Time for Reactors IVA & IVB - with PO_4 addition

above 700 g/d/m3.

The temperature of the reactors was maintained at about 30 degrees Celsius. The influent and effluent pH values were around neutral (see Figure 5.19 to 5.21).

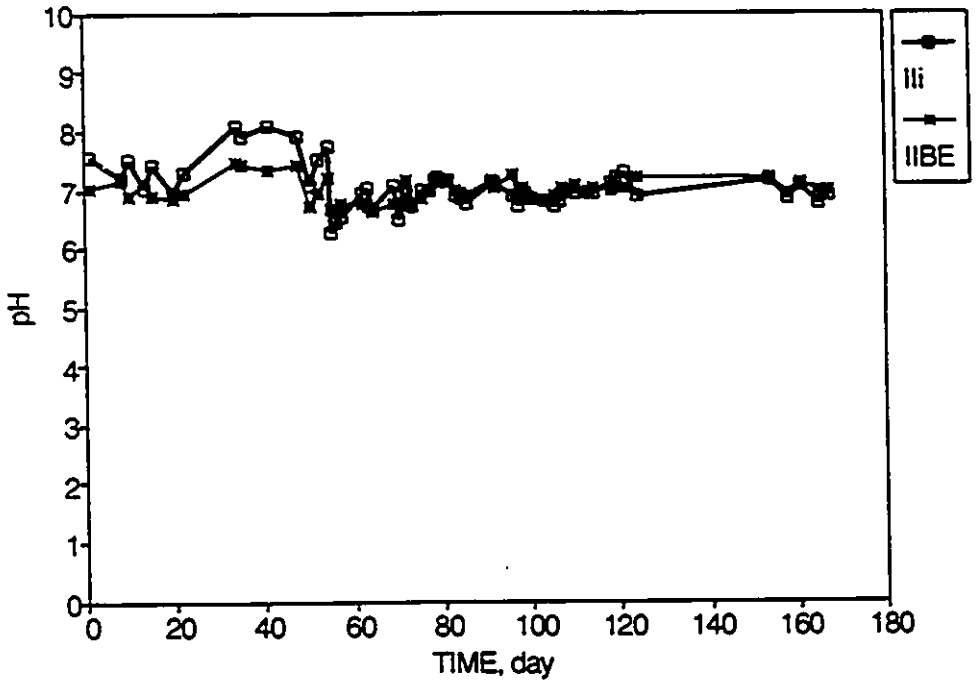


Figure 5.19
Influent and Effluent pH Values versus Time for Reactor IIB - with PO_4 addition

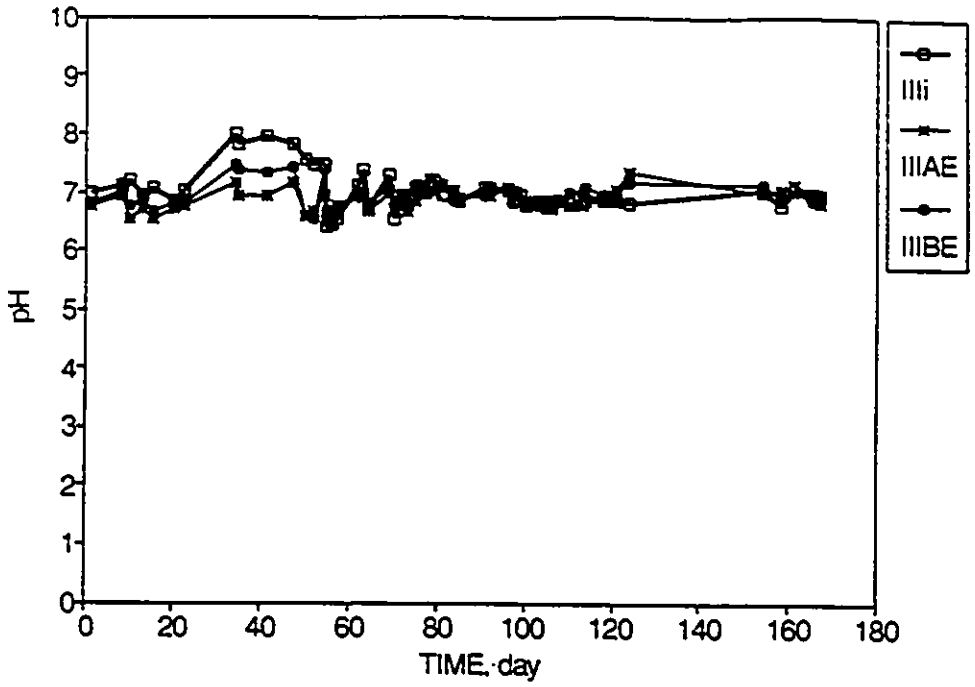


Figure 5.20
Influent and Effluent pH Values versus Time for Reactors IIIA & IIIB - with PO_4 addition

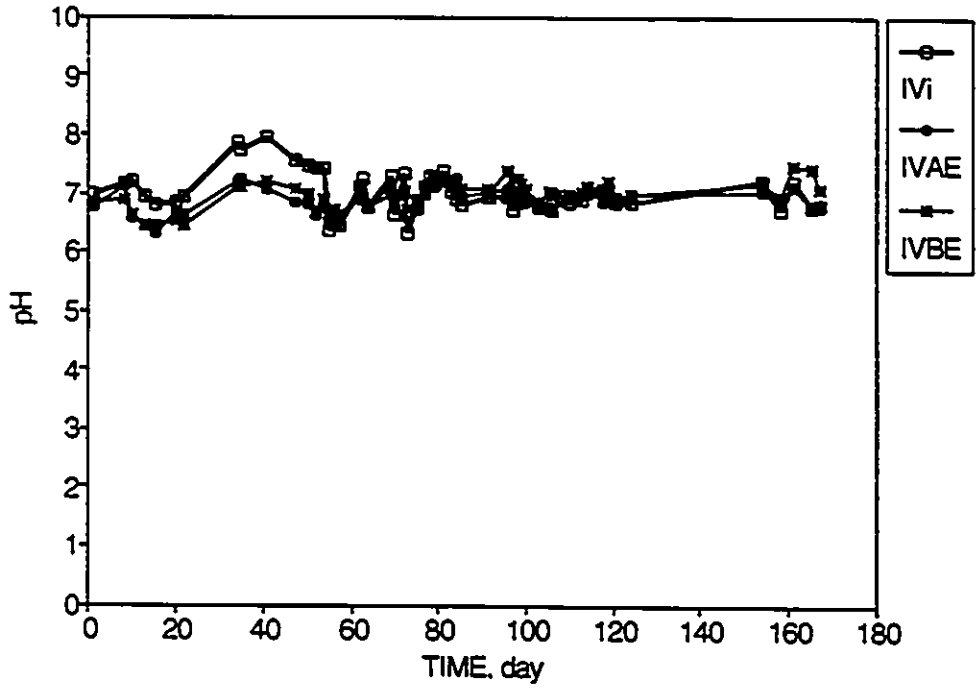


Figure 5.21
Influent and Effluent pH Values versus Time for Reactors IVA & IVB - with PO_4 addition

Figures 5.22 to 5.24 show that sulfide production rate increased with the lactate loading rate. A comparison of these results with PO_4 addition with those in Figures 5.10 to 5.12 without PO_4 addition, a dramatic changes in the sulfide production rates are observed. Table 5.2 illustrates these changes.

Table 5.2
Sulfide Production Rate with and without Phosphate Addition

Reactor	**Sulfide Production Rate**	
	without PO_4	**with PO_4**
IIB	40 g/d/m3	280 g/d/m3
IIIA	70 g/d/m3	230 g/d/m3
IIIB	50 g/d/m3	220 g/d/m3
IVA	90 g/d/m3	280 g/d/m3
IVB	80 g/d/m3	230 g/d/m3

With a phosphate addition of 0.18 g/L, the anaerobic filters were able to increase the sulfide production rate by 3-4 times the values obtained without addition. Table 5.3 shows the number of active bacteria in the reactor after phosphate addition. All reactors displayed much higher bacterial count than when the tap water was the only phosphate source.

Table 5.3
Bacterial Count (cells/mL)- with PO_4 addition

Reactor		IIIA	IVA
Bacterial Count, cells/mL		10^7	10^7-10^8
Reactor	IIB	IIIB	IVB
Bacterial Count, cells/mL	10^7	10^8	10^7-10^8

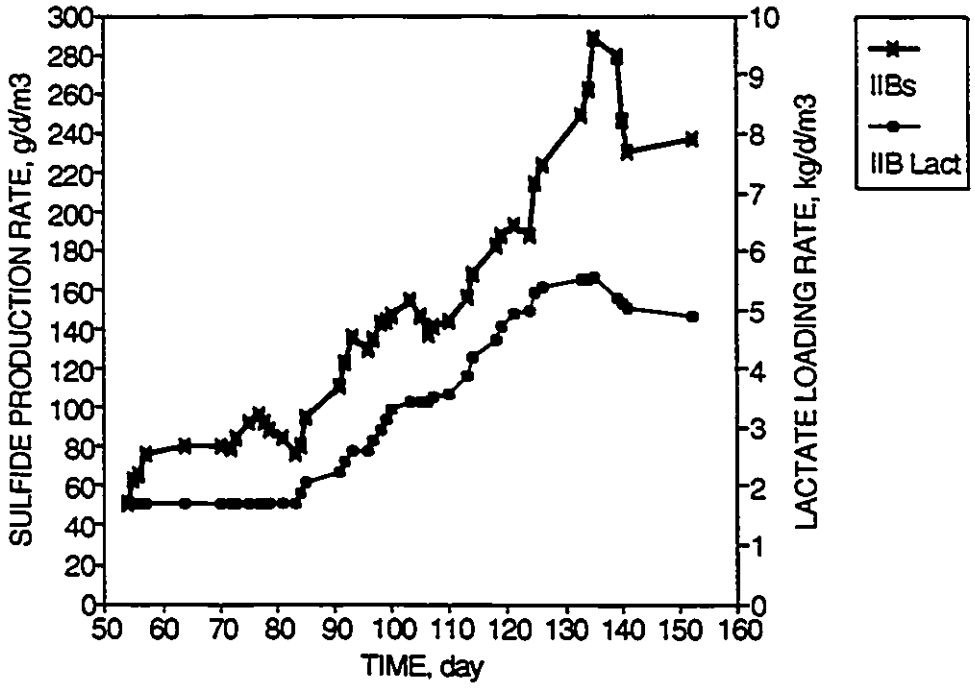


Figure 5.22
Sulfide Production Rate and Lactate Loading Rate versus Time for Reactor IIB - with PO_4 addition

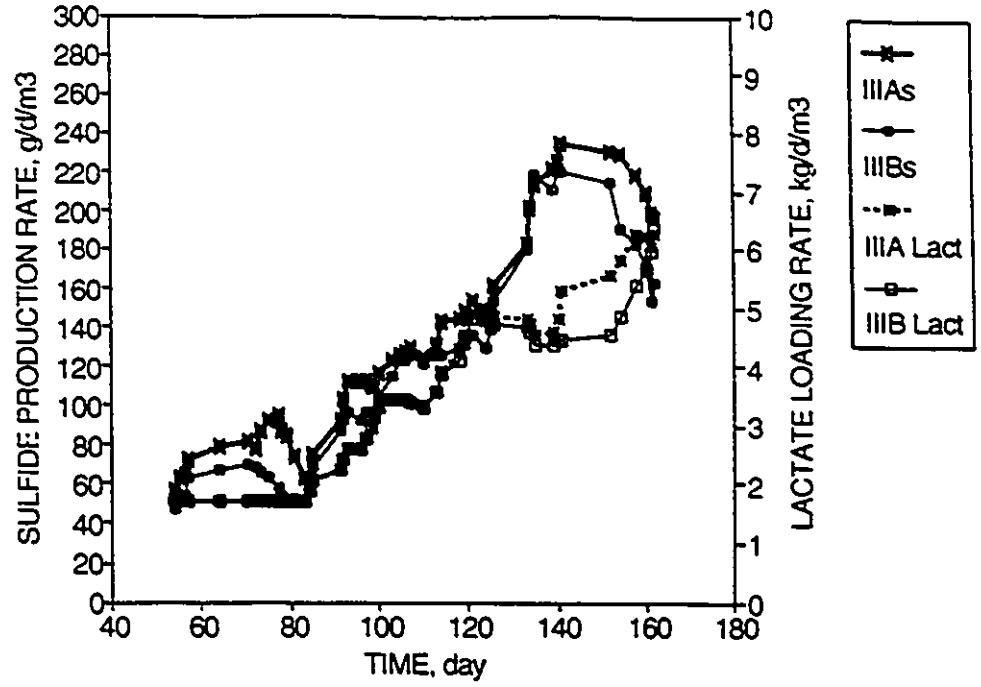


Figure 5.23
Sulfide Production Rate and Lactate Loading Rate versus Time for Reactors IIIA & IIIB - with PO_4 addition

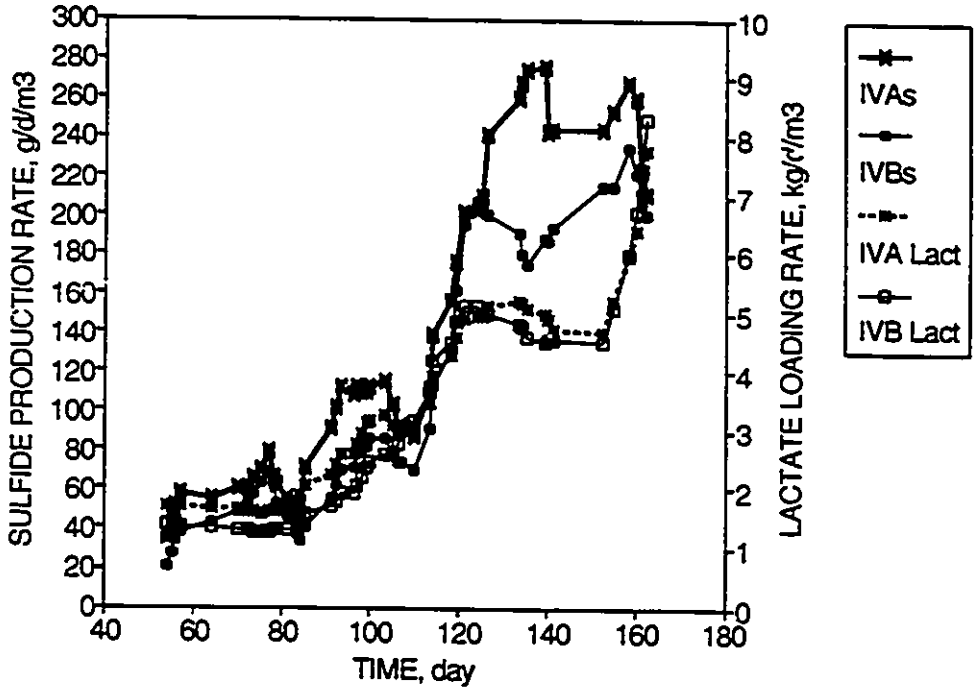


Figure 5.24
Sulfide Production Rate and Lactate Loading Rate versus Time for Reactors IVA & IVB - with PO_4 addition

The relationship between sulfide production rate and lactate loading rate with and without phosphate is plotted in Figure 5.25. The sulfide production rate increased linearly with an increase in lactate loading rate until a maximum rate was attained. After achieving that level, further addition of lactate did not influence the sulfide production rate. The maximum sulfide production rate was obtained at a lactate loading of 6 kg/d/m3 with phosphate addition, and at a lower lactate loading of 2 kg/d/m3, without phosphate addition. The best fit (least squares) for both curves are described by Equations 5.4 and 5.5:

With PO_4 (R-squared = 0.854):

$$R_s = 39.99\ R_L^{0.908} \qquad (5.5)$$

Without PO_4 (R-squared = 0.582):

$$R_s = 18.58\ R_L^{0.641} \qquad (5.4)$$

Equation 5.5 had higher slope than Equation 5.4 indicating higher mass of sulfide production per unit mass of lactate with the addition of phosphate. This study confirms that addition of sufficient nutrients, phosphate in particular, is essential for the biological sulfate reduction. The addition of 0.18 g/L phosphate had increased the sulfide production rate to four times the rate

obtained without phosphate addition . The number of active bacteria had all increased to 10^{7} in all the reactors.

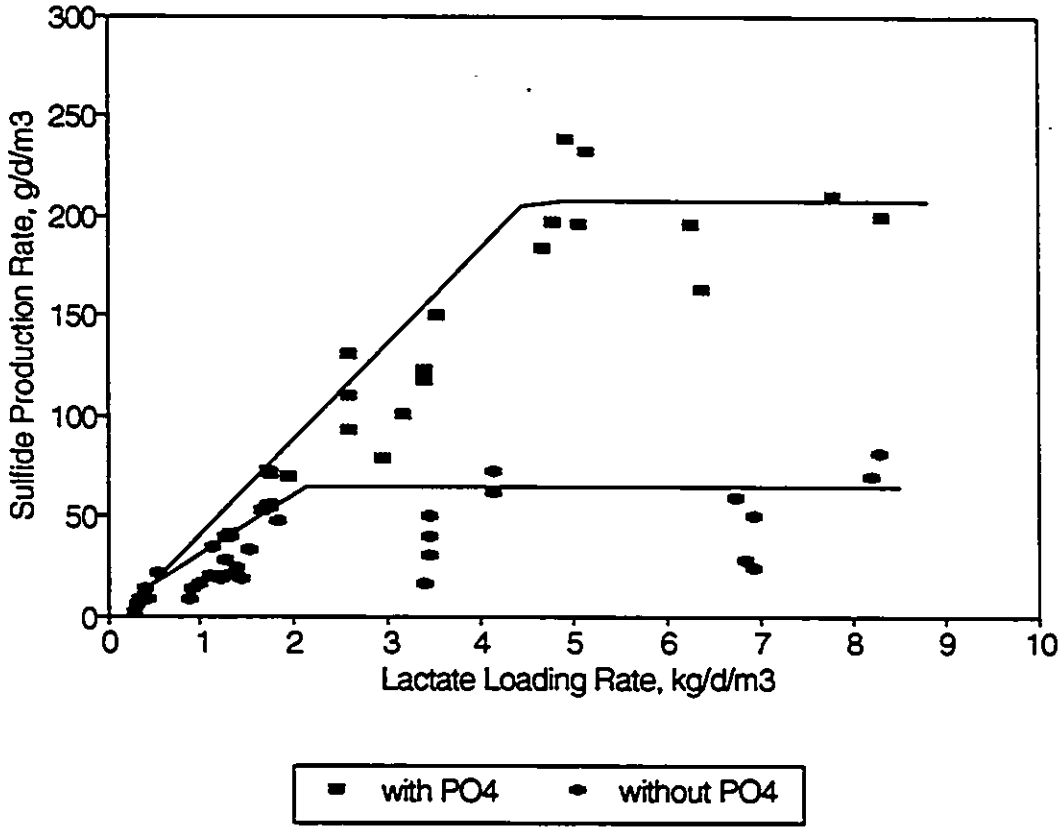


Figure 5.25
Sulfide Production Rate versus Lactate Loading Rate, with and without PO_4 addition

5.3 Material Balance for Sulfate Reduction with Lactate

From the above discussion, it was concluded that the addition of 0.18 g/L phosphate had increased the sulfide production significantly. Consequently analyses for the material balance and consumptive ratio for sulfate reduction with lactate were carried out on the data obtained during the phosphate addition study.

The consumptive ratio is defined as the ratio of the total quantity of an organic chemical consumed during sulfate reduction to the stoichiometric requirement for sulfate reduction and deoxygenation alone. A consumptive ratio of one would indicate that no chemical was required for bacterial synthesis. A ratio greater than one is expected in bacterial synthesis. The higher the ratio, the greater is the requirement of that chemical for biological growth [McCarty et al., 1969].

Table 5.4 lists the half reactions for the oxidation of the organic compounds and the reduction of sulfate and oxygen [McCarty et al., 1969]. Also included is a half reaction for the formation of bacterial cells, using typical empirical formulation $C_5H_7O_2N$ [McCarty et al., 1969]. The half reactions are written on an equivalent basis so that an oxidation and a reduction equation can be directly added.

The consumptive ratio (C_R) was estimated from experimental data, using the following equation and the equivalent concentration indicated in Table 5.4.

Table 5.4
Half Reaction and Milliequivalents of Chemical Change

Equation	Half Reaction	Concentration Change equal to a Milliequivalent per Liter of Chemical Change
Oxidation Equation:		
a) Lactate	$^1/_{12}\ C_3H_5O_3^- + {}^1/_3\ H_2O \text{ ---> } {}^1/_6\ CO_2 + {}^1/_{12}\ HCO_3^- + H^+ + e^-$	3 mg/L org-C
Reduction Equation:		
b) Oxygen	$^1/_4\ O_2 + H^+ + e^- \text{ ---> } {}^1/_2\ H_2O$	8 mg/L Oxygen
c) Sulfate	$^1/_8\ SO_4^{--} + H^+ + e^- \text{ ---> } {}^1/_2\ H_2O + {}^1/_8\ S^{--}$	6 mg/L SO_4
Cell Synthesis:		
d) Cells	$^5/_{28}\ CO_2 + {}^1/_{28}\ NO_3^- + {}^{29}/_{28}\ H^+ + e^- \text{ ---> } {}^1/_{28}\ C_5H_7O_2N + {}^{11}/_{28}\ H_2O$	$^{15}/_{\cdot}$ mg/L org-C

$$C_R = \frac{\text{Equivalent Decrease in Total Organic Carbon}}{\text{Equivalent Decrease in } SO_4 \text{ and } O_2} \qquad (5.6)$$

The consumption of an organic compound after addition to SRB culture was evaluated by measuring the decrease in total organic carbon rather than measuring the decrease in the dissolved organic carbon. It was assumed that lactate, the sole organic source in this study, would totally dissolve in the influent container. Therefore, the total organic carbon would be equal to the dissolved organic carbon that was available to the bacteria.

Table 5.5 displays the consumptive ratios obtained for all reactors. Further details for the consumptive ratio calculations are given in Appendix IV.

Table 5.5
Consumptive Ratios Obtained in Different Reactors

Reactor	Average Consumptive Ratio C_R
IIB	1.0
IIIA	1.4
IIIB	1.5
IVA	1.0
IVB	1.0
Overall Average C_R = 1.2 ± 0.2	

The high standard deviation of 0.2 for C_R was caused by the dynamic and unique characteristics of bacterial activity in each reactor. The overall average consumptive ratio of 1.2, indicates that 17%

[(1.2-1)/1.2 *100%] of organic used was for cell synthesis, and 83% for reduction and deoxygenation.

The following balanced equations for the overall sulfate reduction are obtained by using the half reactions from Table 5.4. The equation for sulfate reduction is obtained by adding Equations a and c:

$$^1/_{12}\ C_3H_5O_3^- + {}^1/_8\ SO_4^{--} \longrightarrow {}^1/_6\ H_2O + {}^1/_8\ S^{--} + {}^1/_6\ CO_2 + {}^1/_{12}\ HCO_3^- \qquad (5.7)$$

Similarly, bacterial cell synthesis is obtained by adding Equations a and d:

$$^1/_{12}\ C_3H_5O_3^- + {}^1/_{28}\ NO_3^- + 0.01\ CO_2 + 0.036\ H^+ \longrightarrow 0.06\ H_2O + {}^1/_{12}\ HCO_3^- + {}^1/_{28}\ C_5H_7O_2N \qquad (5.8)$$

By adding Equation 5.7 and 5.8, the overall sulfate reduction equation is derived:

$$SO_4^{--} + 1.33\ C_3H_5O_3^- + 0.288\ NO_3^- + 0.288\ H^+ \longrightarrow 0.288\ C_5H_7O_2N + 1.816\ H_2O + S^{--} + 1.256\ CO_2 + 1.33\ HCO_3^- \qquad (5.9)$$

Thus,

10 mg/L	+	12.3 mg/L	=	3.39 mg/L	+	3.33 mg/L
Sulfate		Lactate		Cells		Sulfide

The following material balance for the overall deoxygenation (required prior to reduction) was obtained in a similar manner.

$$O_2 + 0.67\ C_3H_5O_3^- + 0.14\ NO_3^- + 0.14\ H^+ \rightarrow \quad (5.10)$$
$$0.67\ H_2O + 0.63\ CO_2 + 0.67\ HCO_3^- + 0.24\ H_2O + 0.14\ C_5H_7O_2N$$

Thus,

10 mg/L + 18.6 mg/L = 4.94 mg/L

DO Lactate Cells

The theoretical quantity of lactate required for sulfate reduction can be computed from Equations 5.9 and 5.10. The stoichiometric amounts can be expressed on a mass basis as shown in Equation 5.11.

$$C_{lt} = 1.23\ C_{si} + 1.86\ DO \quad (5.11)$$

Where,

C_{lt} = Theoretical lactate requirement concentration, mg/L

C_{si} = Initial SO_4 concentration, mg/L

DO = Initial dissolved oxygen concentration, mg/L

Since in this experiment not all of the incoming sulfate concentration was converted, equation 5.11 can be modified to become:

$$C_{Lt} = 1.23 \ (C_{si} - C_{st}) + 1.86 \ DO \qquad (5.12)$$

Where,

C_{st} = Final SO_4^{--} concentration, mg/L

Theoretically, the observed lactate requirement should be equal to the computed lactate requirement, ie:

$$C_{Lm} / C_{Lt} = 1$$

Where,

C_{Lm} = Measured lactate requirement, mg/L

Table 5.6 lists the ratio of C_{Lm} to C_{Lt} obtained in these experiments. The initial dissolved oxygen concentration was 8 mg/L.

Table 5.6
C_{Lm}/C_{Lt} Values for Different Reactors

Reactor	**C_{Lm}/C_{Lt}**
IIB	0.90
IIIA	1.19
IIIB	1.32
IVA	0.93
IVB	0.91

Overall Average C_{Lm}/C_{Lt}= 1.05 ± 0.2

The overall average ratio of 1.05 for C_{Lm}/C_{Lt} indicates that

Equation 5.12 can be used with confidence to calculate the lactate requirements.

It should be noted that the denominator in Equation 5.6 for C_r does not take into account the bacterial synthesis requirement, while in calculating the ratio C_{Lm}/C_L, the denominator includes the bacterial synthesis requirements. The numerators in both cases are total organic carbon used by the bacteria and as such includes the organic required for bacterial synthesis. Therefore, the ratio Cr is expected to be equal or greater than one, on the other hand C_{Lm}/C_L must be equal to one.

Figure 5.26 plots the relationship between the sulfide produced versus total organic carbon (TOC) utilized. There exists a linear relationship. The higher was the amount of the TOC used by the SRB, the higher was the sulfide production. Equation 5.13 shows the correlation between the two variables, with R-squared=0.804.

$$S_m = 0.755 \text{ TOC utilized} - 2.23 \qquad (5.13)$$

Where,

S_m = Measured sulfide production, mg/L

TOC utilized = TOC influent- TOC effluent, mg/L

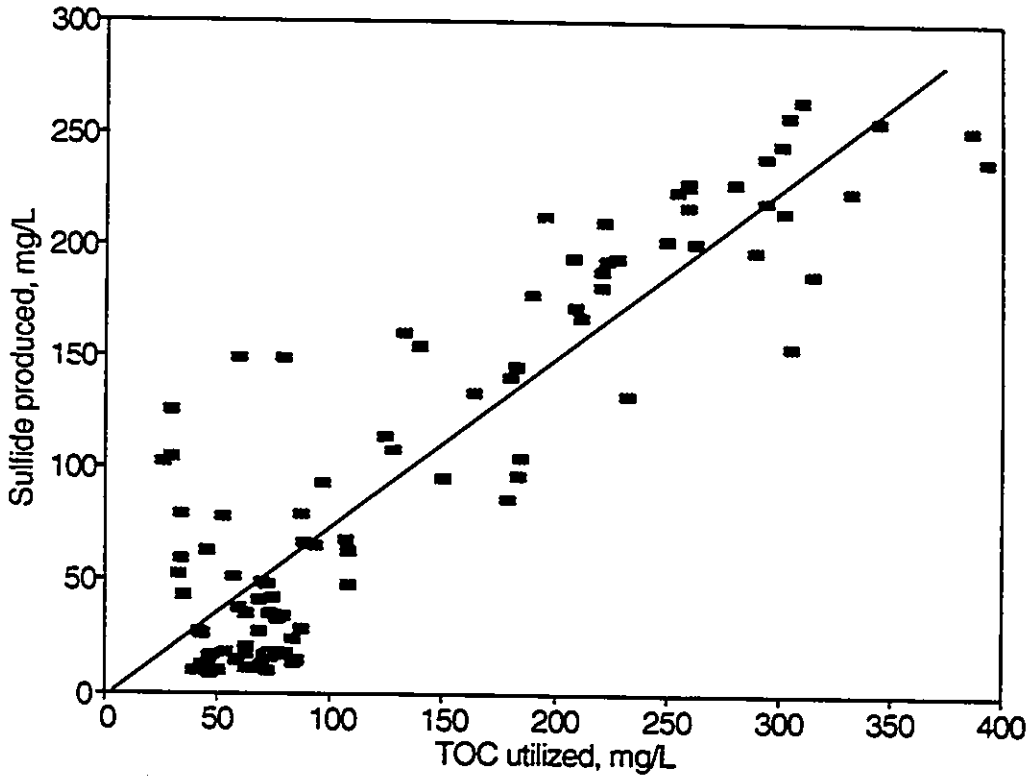


Figure 5.26
Sulfide Production versus Total Organic Carbon Utilized by Sulfate Reducing Bacteria (SRB)

However, sulfide production can also be predicted from theoretical sulfide production obtained from Equation 5.9.

$$S_t = 3.33/12.3\ C_{ut} \qquad (5.14)$$

Where,

S_t = Theoretical sulfide production, mg/L

The ratios between theoretical and measured sulfide production obtained in this study are shown in Table 5.7.

Table 5.7
Ratio S_m/S_t for Different Reactors

Reactor	**S_m/S_t**
IIB	0.96
IIIA	1.26
IIIB	1.4
IVA	0.99
IVB	0.96

Overall Average S_m/S_t = 1.11 ± 0.2

The overall average ratios of S_m/S_t and C_{ut}/C_{ut} obtained in this study were slightly higher than one, because the theoretical calculations did not take into consideration the possibility of incomplete degradation of organic compound. Desulfovibrio, the species of SRB that utilize lactate as carbon and energy source (see Equation 3.1), have a very limited capacity to degrade organic

carbon. They scavenge hydrogen with high affinity and use it as electron donor or carry out incomplete oxidation of lactate. All incomplete oxidations ultimately result in the formation of acetate. Unless, Desulfotonaculum, acetate oxidizing SRB (see Equation 3.4), are present, only 33% of organic matter can be degraded completely.

Therefore, the theoretical lactate requirement and sulfide production agree with the measured values. The consumptive ratio indicates that the organic compound was used not only for sulfate reduction and deoxygenation, but also for bacterial synthesis.

5.4 Heavy Metal Loadings

It was shown in the previous section that the optimum sulfide production achieved with 0 18 g/L phosphate addition and 6 kg/d/m3 lactate loading. This optimum operating condition was used in the heavy metal removal study. The heavy metals included lead (Pb), chromium (Cr), copper (Cu) and cadmium (Cd), and were applied separately.

Reactor IA was a non-bacterial control. It monitored the non-microbial heavy metal removal such as hydroxide and carbonate precipitation, chelation by organic and inorganic ligands [Rivera, 1983; Chian et al., 1983]. The dissolved metals will not be removed as precipitate metal sulfides in the Control Reactor, since sulfides were the microbial product of sulfate reducing bacteria (SRB). Figure 5.27 shows the absence of SRB in the Control Reactor

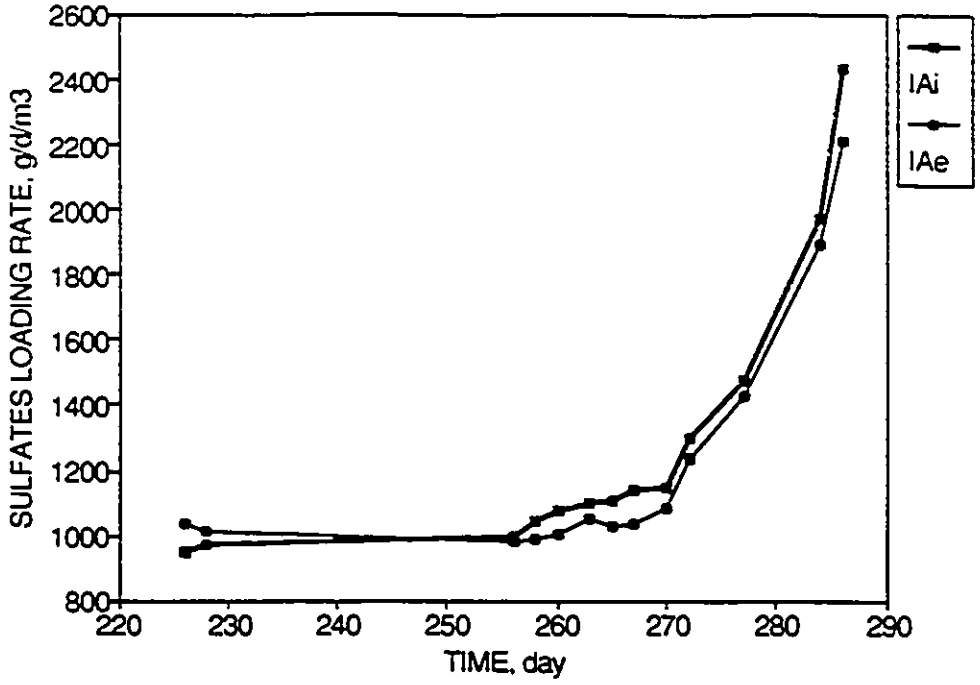


Figure 5.27
Influent and Effluent Sulfate Loading versus Time for Reactor IA (ControL)

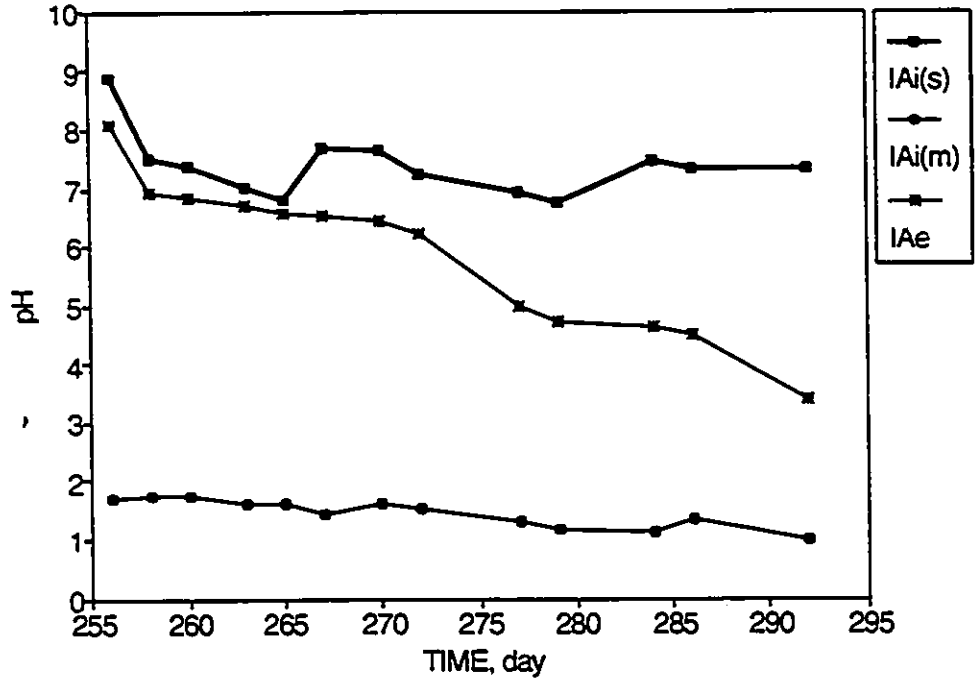


Figure 5.28
Influent (Substrate Line and Metal Line) and Effluent pH Values versus Time for Reactor IA (Control)

because there is zero sulfate reduction. Figure 5.28 displays the influent and effluent pH in the Control Reactor. The influent consisted of two separate feed lines, substrate feed line and metal feed line. Subscript "i(s)" represents substrate line and "i(m)" stands for metal line. The substrate pH remained around 7 and 8, while the metal feed pH ranged between 1 and 2. After the two feeds were mixed in the reactor, the effluent pH ranged from 3 to 7. There was no buffering capacity in the reactor.

The bacterial dissolved metal removal included sulfide and carbonate precipitations because sulfide and carbonate were the product of SRB. However, at a pH of less than 7 the sulfides would determine the soluble heavy metal concentration, while carbonate would determine the soluble concentration at higher pH value [DeWalle et al., 1979]. Therefore, sulfide precipitation would be the predominant way in this study.

Reactor IIB was used as a bacterial control unit. Its purpose was to monitor the sulfate reduction in the absence of heavy metals. The sulfates were reduced at a constant rate of 700 g/d/m3, as depicted in Figure 5.29. The effluent pH was maintained at 7 and 8 (Figure 5.30).

Lead, chromium, copper, and cadmium were dissolved in appropriate amounts and mixed to make the synthesis metal solution to be treated in the control reactor, IA. However, the results are dicussed for individual metals with their counterpart results obtained from the microbial metal removal studies.

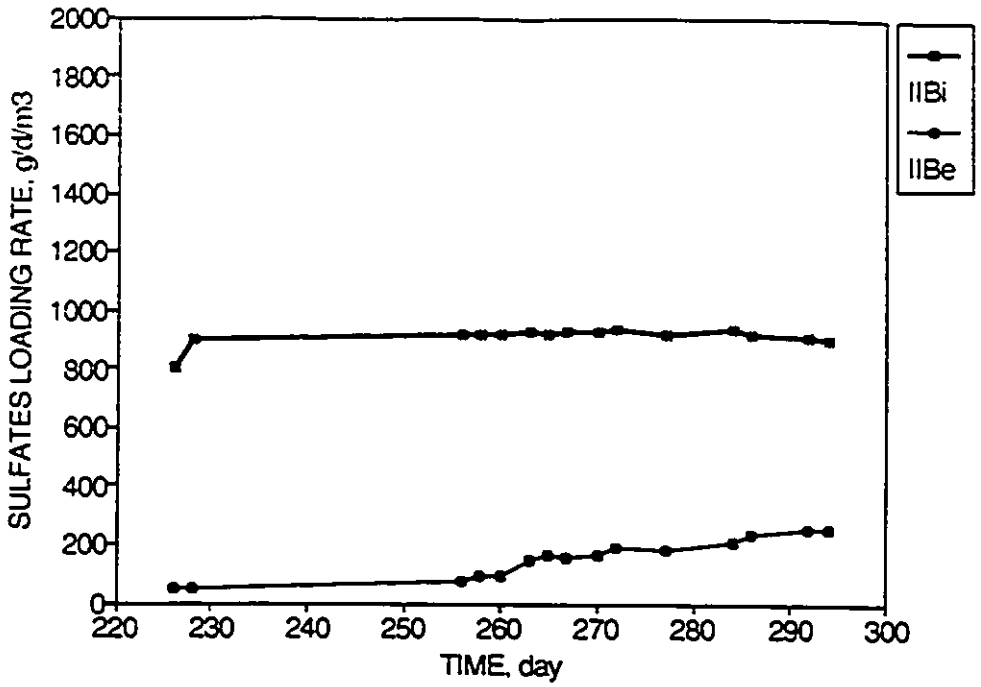


Figure 5.29
Influent and Effluent Sulfate Loading versus Time for Reactor IIB

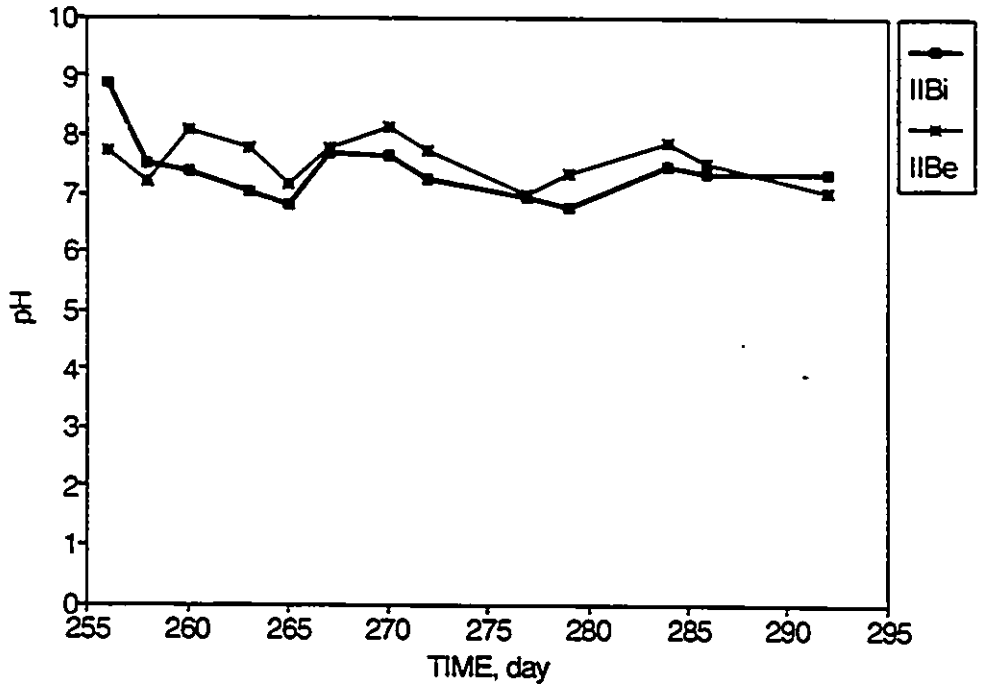


Figure 5.30
Influent and Effluent pH Values versus Time for Reactor IIB

5.4.1 Lead

Reactor IIIA was operated to study lead removal. Figure 5.31 shows influent and effluent dissolved and total lead concentrations versus time. The excess sulfide concentration is also plotted to indicate the availability of free sulfide. The dissolved and total lead concentrations were identical in the influent. Thus, the influent contained no suspended lead. After passing through the reactor, most of the lead had been precipitated as shown by a very low dissolved lead concentration in the effluent. A part of precipitated lead had settled in the reactor and the remaining was carried in the effluent. This is confirmed by a higher total lead concentration than the dissolved lead concentration in the effluent. The presence of 20 mg/L excess sulfide at the end of the study shows the possibility of treating even higher lead concentration.

The results for Control Reactor IA are plotted in Figure 5.32. It should be noticed that the highest lead concentration in the influent to the control was much lower than the one in Reactor IIIA. Even though equal amount of lead sulfate was added in the influent of both reactors, the lead sulfate in the Control Reactor was mixed with other metal sulfates before feeding. The mixing with other metal sulfates had decreased the solubility of the lead. Therefore, the lead results of Reactor IA only indicate the qualitative behaviour and can not be used to represent the non-bacterial lead removal that occurred in Reactor IIIA.

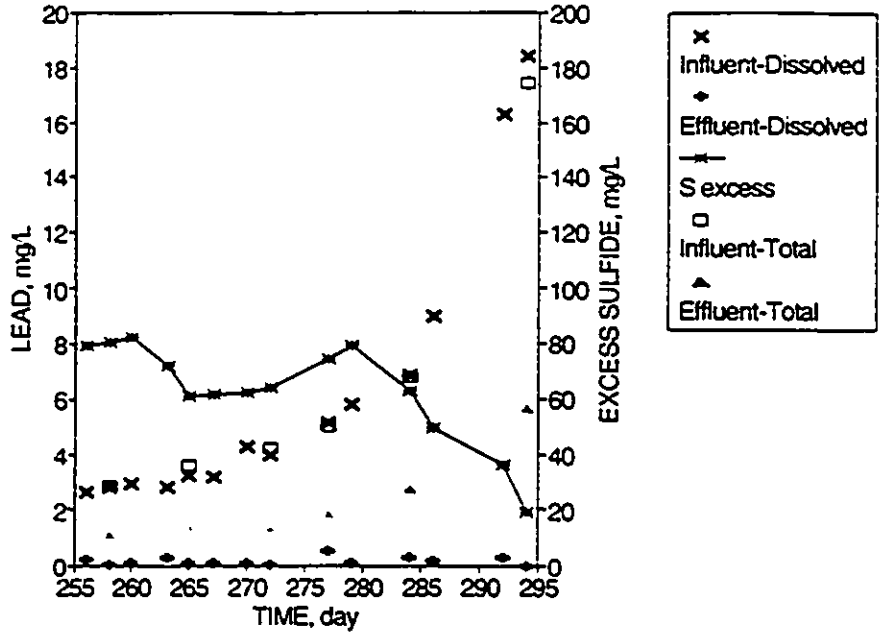


Figure 5.31
Dissolved and Total Lead Concentrations and Excess Sulfide versus Time for Reactor IIIA

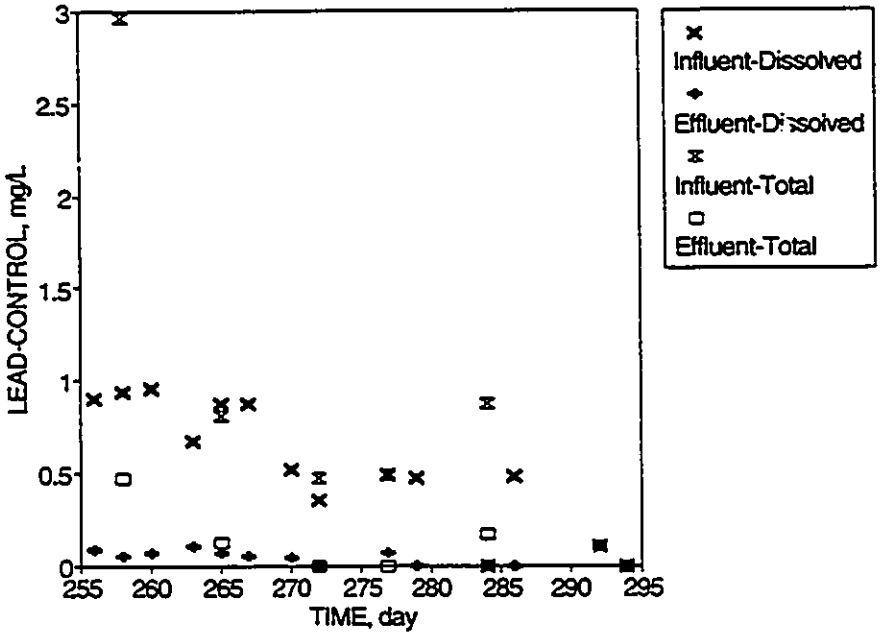


Figure 5.32
Dissolved and Total Lead Concentrations versus Time for Reactor IA

Figure 5.33 shows the dissolved and total removal efficiencies versus lead concentration for Reactor IIIA. The dissolved lead was removed with 90% or greater efficiencies whereas the removal of total lead ranged between 60% to 70%. However, it is apparent that a significant amount of dissolved lead was removed chemically in the absence of sulfide.

The presence of lead in the feed caused no toxicity to the microorganism, as is indicated by a constant sulfate reduction rate in Figure 5.34. The rate of sulfate reduction was approximately 600 g/d/m3, which is only slightly lower than that in Reactor IIB (Figure 5.29). The microorganisms were able to maintain the effluent pH between 7 and 8 (Figure 5.36).

Figure 5.35 exhibits a constant sulfide removal, regardless of the increase in the amount of lead to be removed. The sulfur balance (Table 5.8), showed that the calculated sulfide needed to precipitate lead was lower than the actual sulfide removed. Therefore, the sulfide was removed not only as lead sulfide, but also as other metal sulfides.

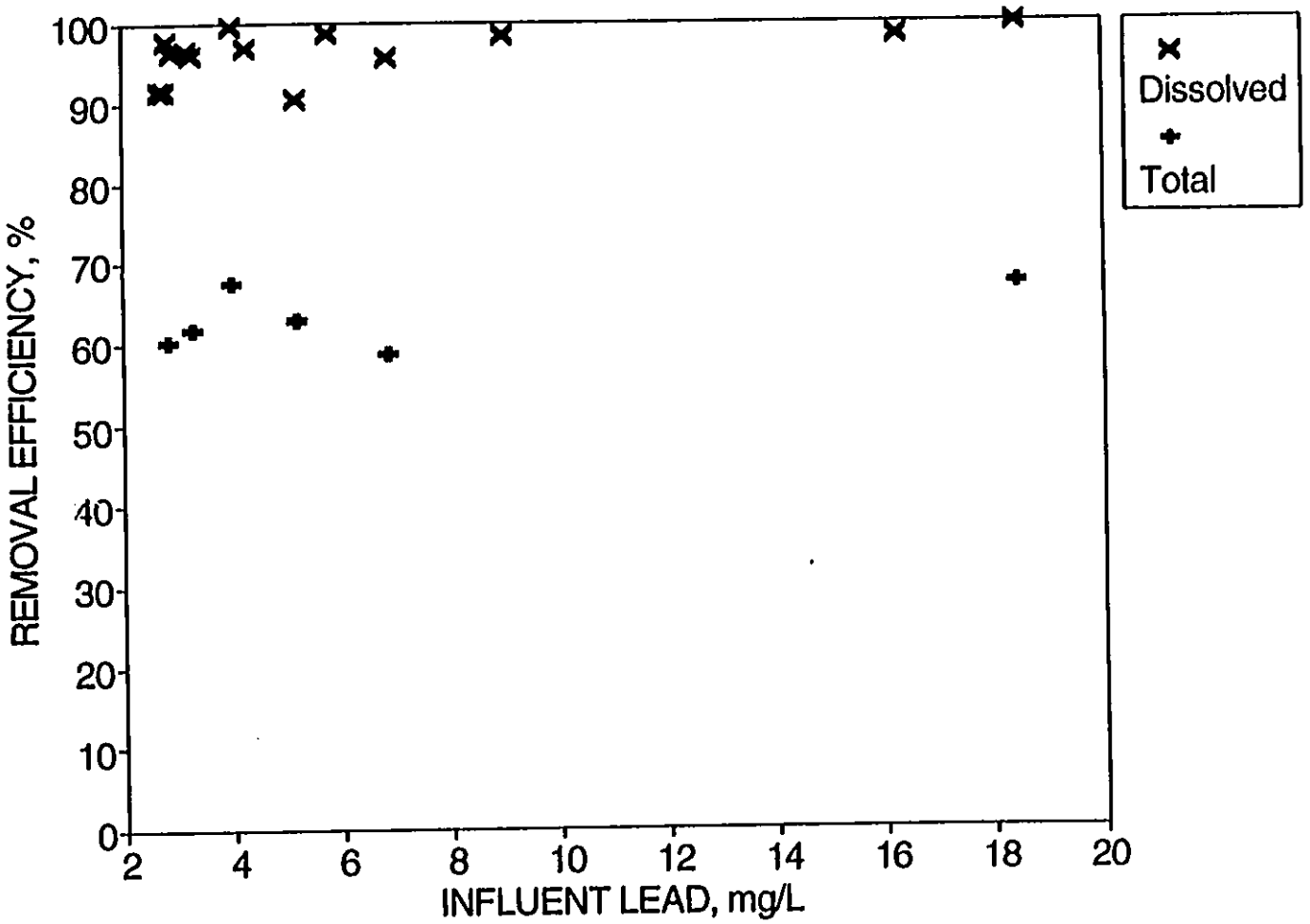


Figure 5.33
Dissolved and Total Lead Removal Efficiencies versus Influent Lead Concentration for Reactor IIIA

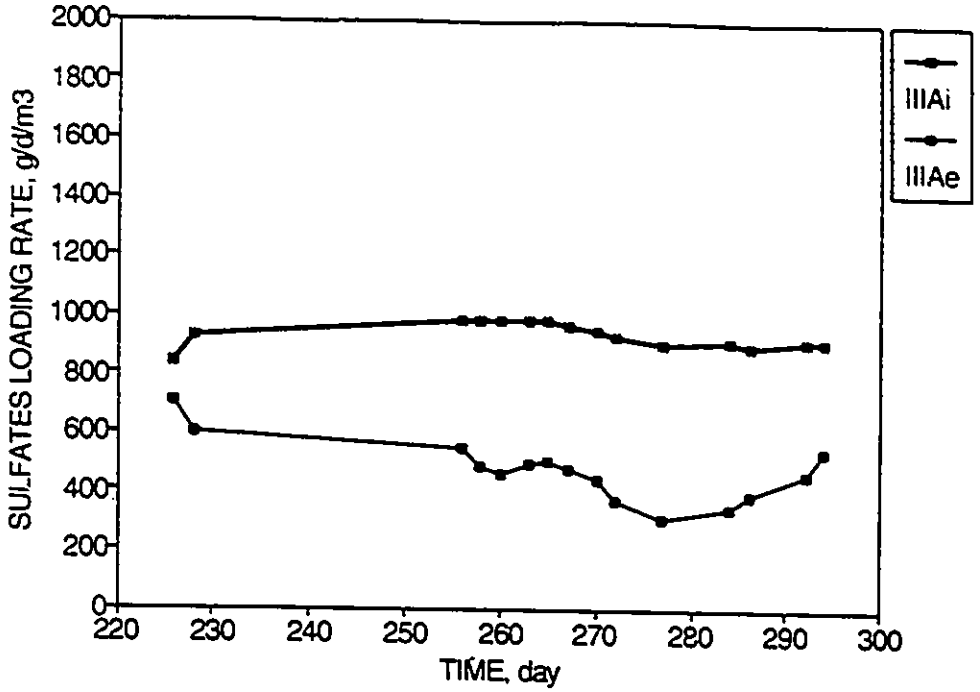


Figure 5.34
Influent and Effluent Sulfate Loading versus Time for Reactor IIIA

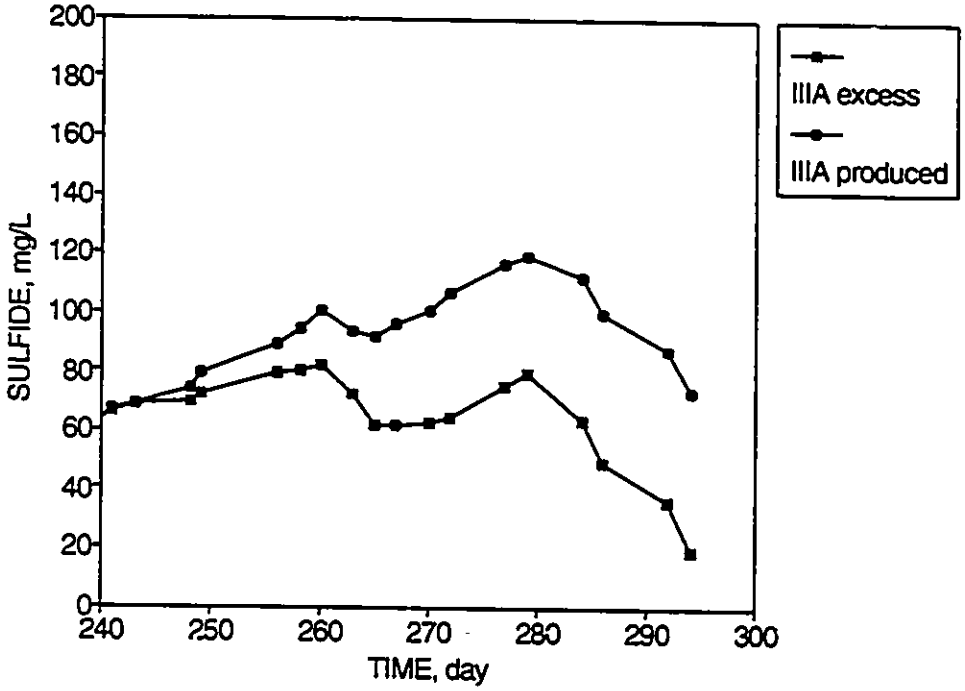


Figure 5.35
Excess Sulfide and Sulfide Produced versus Time for Reactor IIIA

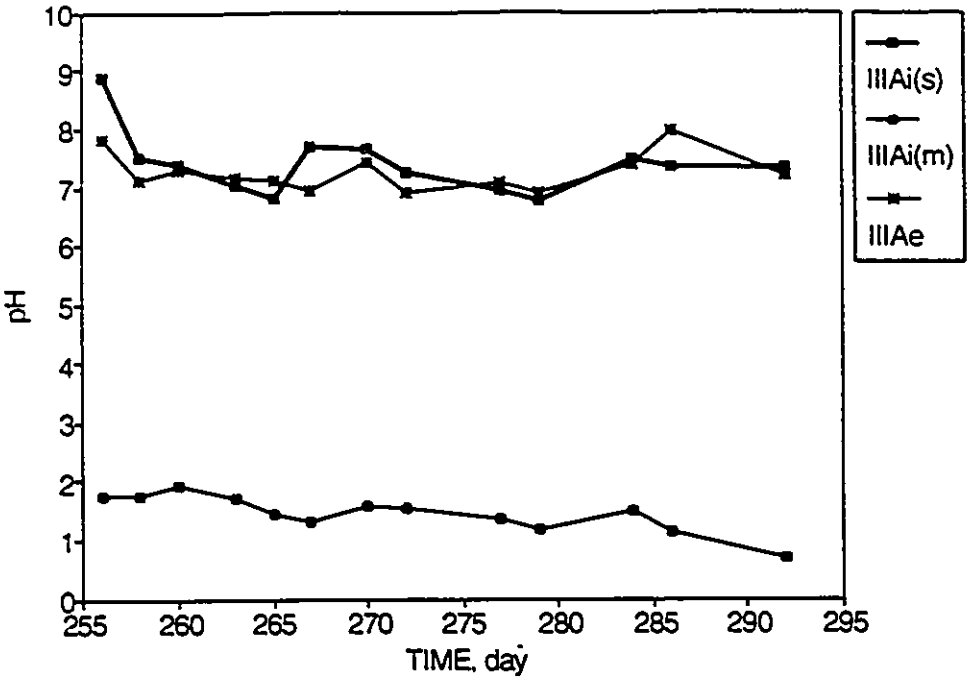


Figure 5.36
Influent (Substrate Line and Metal Line) and Effluent pH Values versus Time for Reactor IIIA

5.4.2 Chromium

Reactor IIIB studied the chromium removal. Figure 5.37 exhibits that all of the chromium in the influent was in the dissolved form and had precipitated after being fed to the reactor. Consequently, a lower chromium concentration was observed in the effluent. All of the precipitated chromium had been removed by the filter, as is indicated by the same amount of total and dissolved chromium in the effluent.

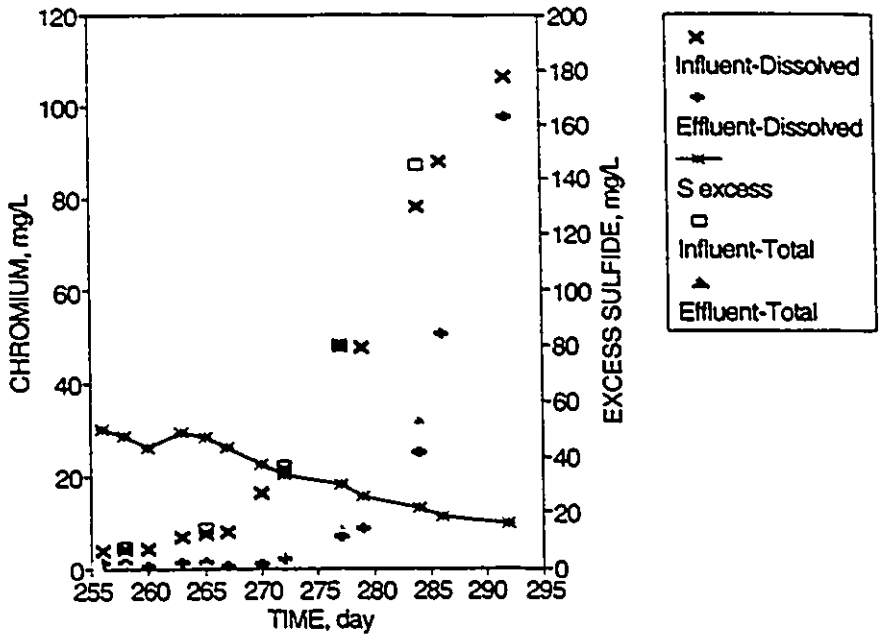


Figure 5.37
Dissolved and Total Chromium Concentrations and Excess Sulfide versus Time for Reactor IIIB

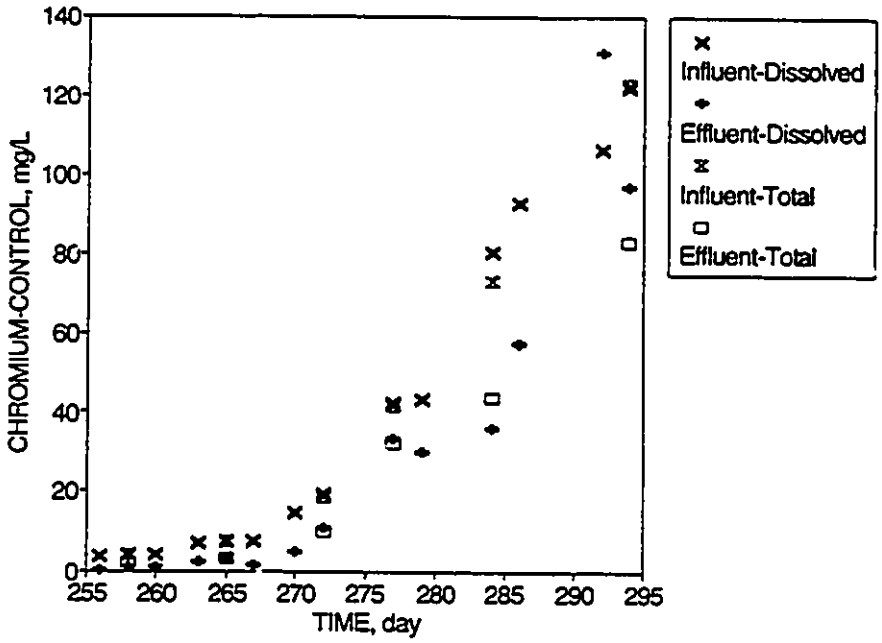


Figure 5.38
Dissolved and Total Chromium Concentrations versus Time for Reactor IA

Figure 5.38 shows the results for the Control Reactor IA. It represents the non-bacterial chromium removal that took place in reactor IIIB. Approximately 40% of the chromium had precipitated in the Control Reactor.

The dissolved, total and bacterial chromium removal efficiencies versus influent chromium concentration are plotted in Figure 5.39. The bacterial metal removal efficiency was the removal efficiency due to metal precipitation with the sulfide. The method for calculating this removal is shown in Appendix IV. The removal efficiency was approximately 50% to 60% with influent chromium concentration up to 45 mg/L. The dissolved and total removal efficiencies had reached 80% to 95%. Lower efficiencies were observed at lower concentrations, which was due to acclimation period. Initial acclimation helped the system to reduce the severity of toxic effect due to subsequent higher metal concentration. At chromium concentrations greater than 45 mg/L, the filter's performances started to decrease. It was also followed by the decrease in the sulfate reduction (see Figure 5.40) and the effluent pH had decreased to below 6 (Figure 5.42). Failure had occurred at chromium concentration of 80 mg/L when the bacterial removal efficiency was only 10%, with the total and dissolved removal efficiencies of 60%. As the bacterial removal efficiency decreased, the sulfide removal also decreased.

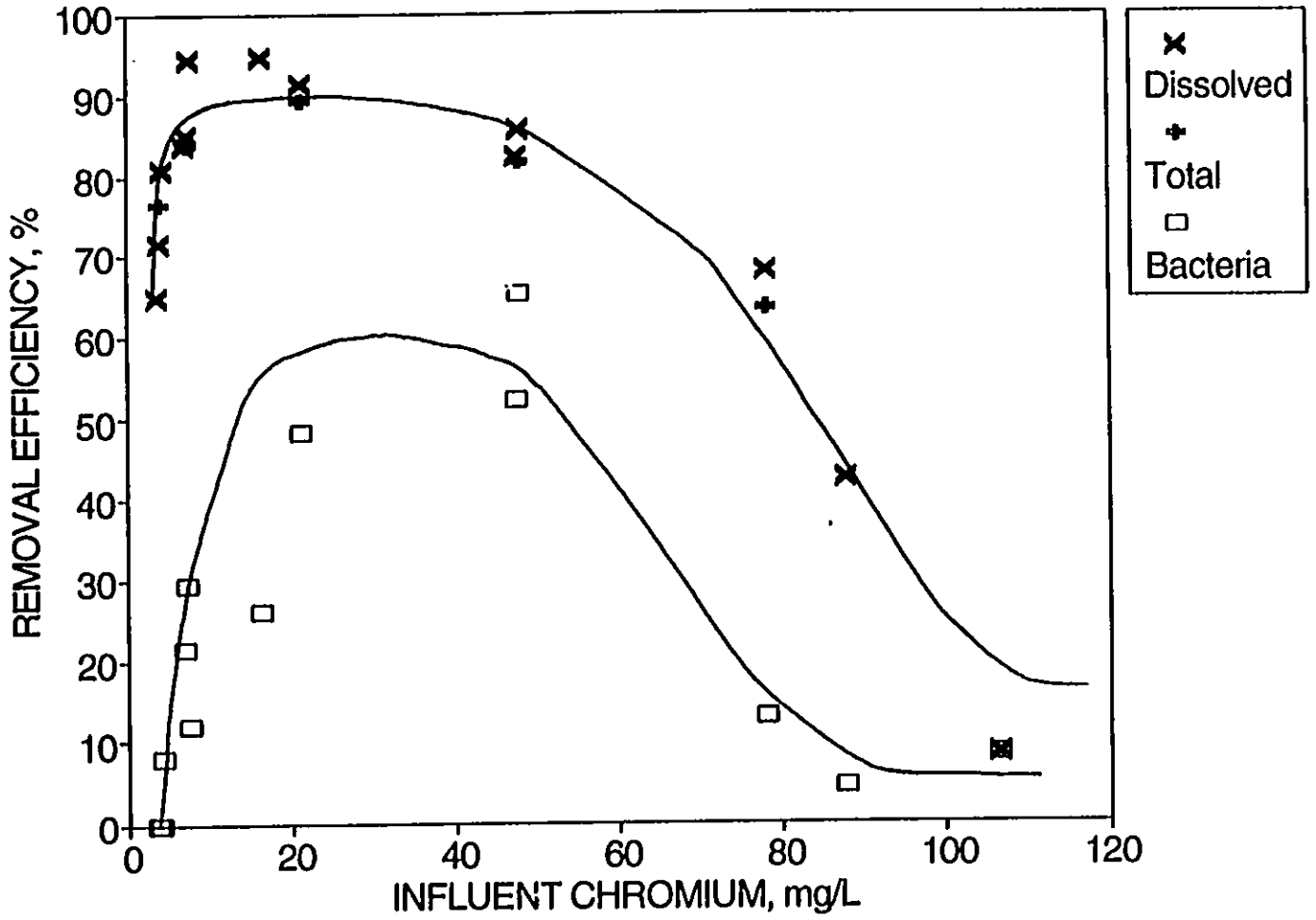


Figure 5.39
Dissolved, Total and Bacterial Chromium Removal Efficiencies versus Influent Chromium Concentration for Reactor IIIB

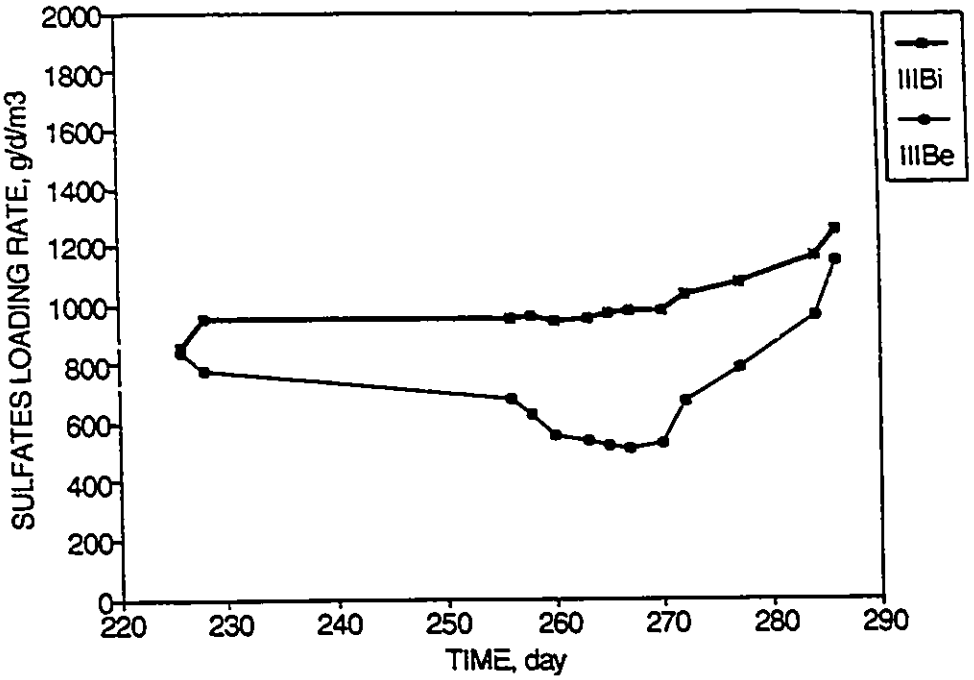


Figure 5.40
Influent and Effluent Sulfate Loading Rates versus Time for Reactor IIIB

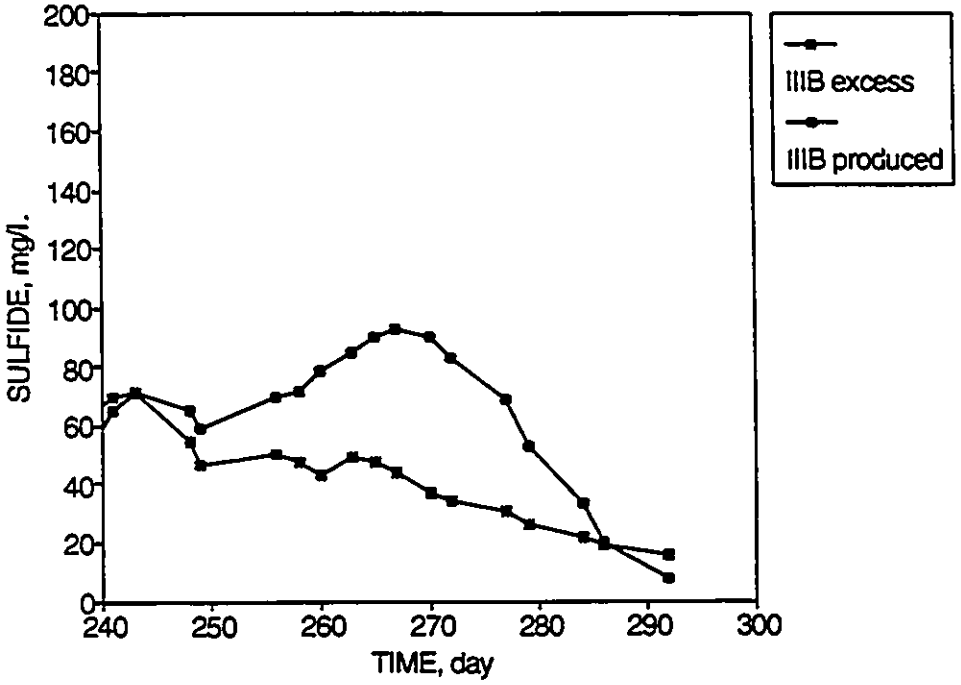


Figure 5.41
Excess Sulfide and Sulfide Produced versus Time for Reactor IIIB

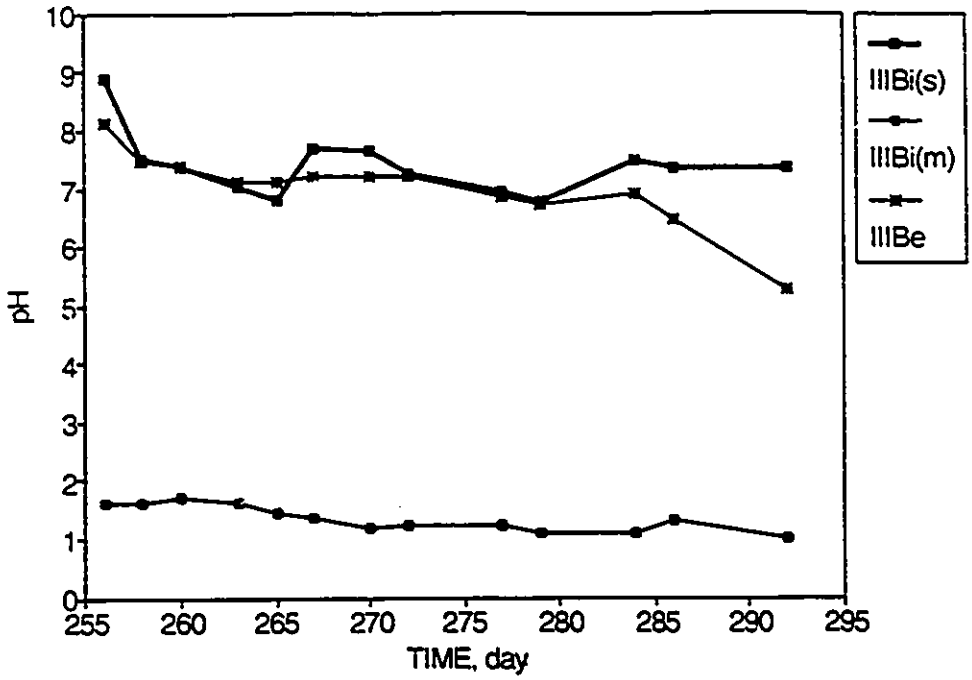


Figure 5.42
Influent (Substrate Line and Metal Line) and Effluent pH Values versus Time for Reactor IIIB

5.4.3 Copper

Reactor IVA was used to investigate the copper removal. Figure 5.43 shows that the amount of total copper was equal to the dissolved copper in the influent. Almost all of the dissolved copper had precipitated and was removed while passing through the reactor. This had resulted in a low copper concentration in the effluent.

Figure 5.44 shows the results for the Control Reactor IA. It depicts the non-bacterial copper removal that occurred in Reactor IVA. Almost all of the copper was removed at below 50 mg/L. After 50 mg/L, the percent removal kept decreasing.

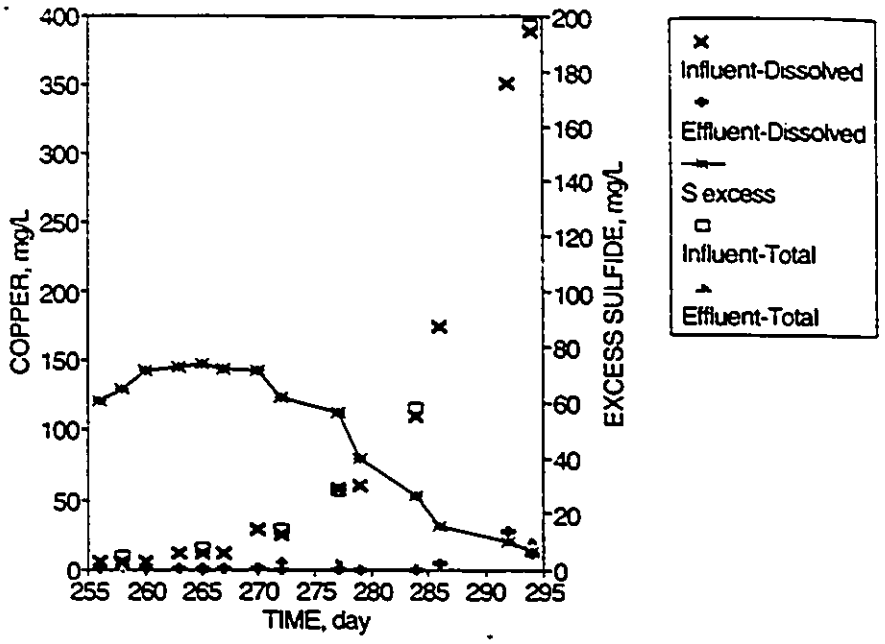


Figure 5.43
Dissolved and Total Copper Concentrations and Excess Sulfide versus Time for Reactor IVA

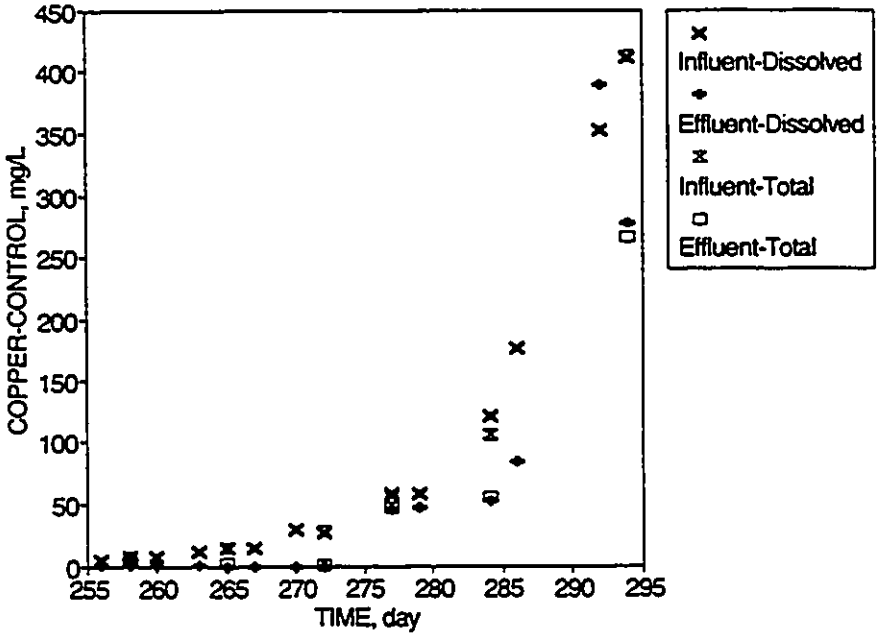


Figure 5.44
Dissolved and Total Copper Concentrations versus Time for Reactor IA

Figure 5.45 displays the dissolved, total and bacterial copper removal efficiencies versus influent concentration. The highest bacterial removal efficiency was 80% at influent copper concentration of 60 mg/L. Initially, below 60 mg/L, the microorganisms were acclimated to the heavy metal. The efficiencies dropped to 50% at a concentration greater than 60 mg/L.The decrease in the bacterial removal efficiency was followed by the decrease in sulfate reduction (Figure 5.46). The drop in sulfate reduction indicates bacterial inhibition. The inhibition was also shown by the inability of the sulfate reducing bacteria (SRB) to maintain their favourable pH, around neutral (Figure 5.48).

The filter was able to achieve 50% bacterial removal efficiency, regardless of the increase in copper concentration. Figure 5.47 shows that, although there was a decrease in the sulfide production, the amount of sulfide produced was sufficient to maintain 50% efficiency up to 400 mg/L.

The dissolved and total removal efficiencies were greater than 90%, regardless of the variations in the bacterial removal efficiencies. Among the heavy metals studied, copper had the highest total removal efficiency. According to DeWalle et al. (1979) of all metals, copper was found to be associated with the largest solid particles. Therefore, the precipitated copper would rapidly settled to the bottom of the filter.

The higher dissolved removal efficiencies, than that of the bacterial removal, suggests that not all the copper was precipitated as copper sulfide.

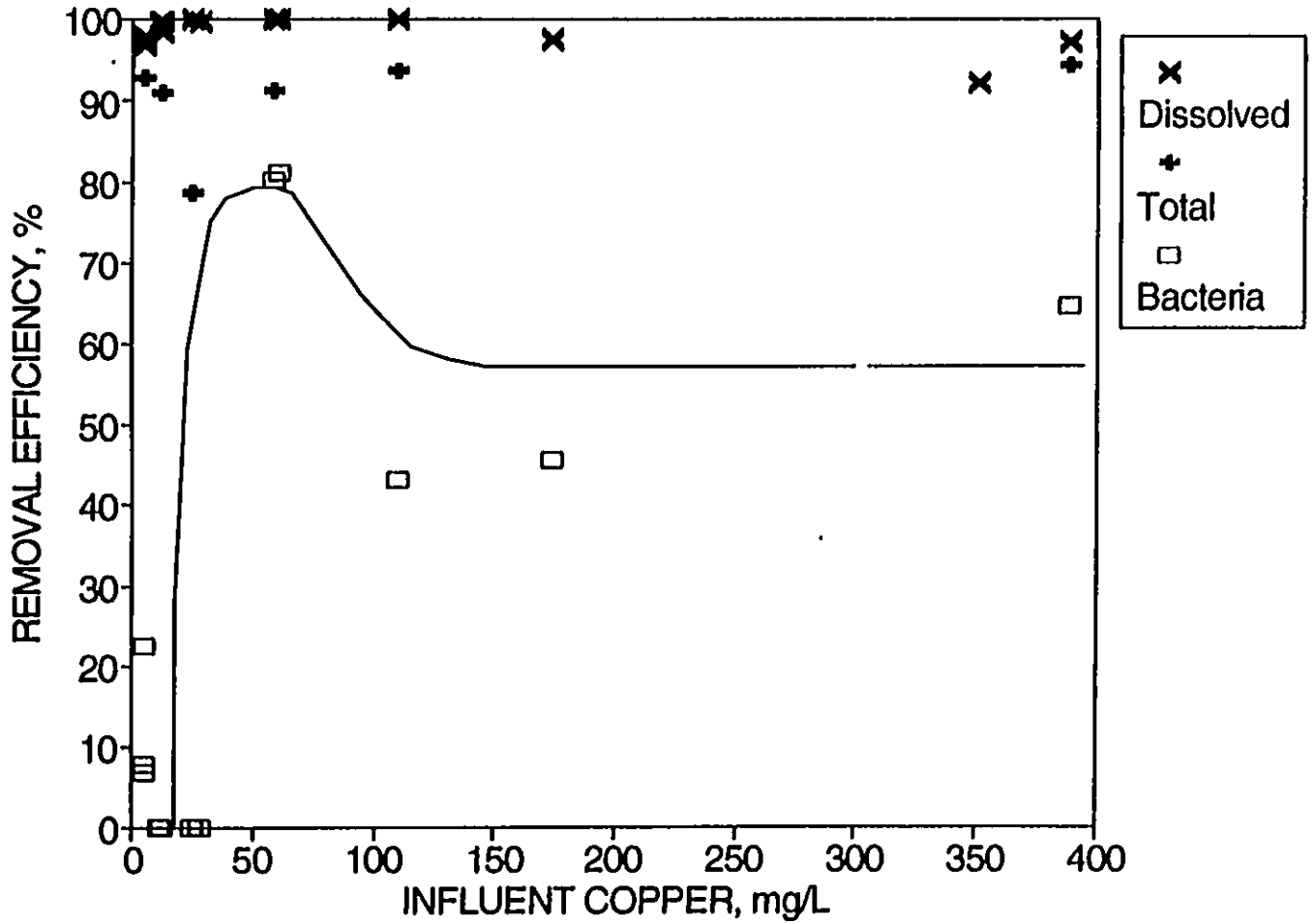


Figure 5.45
Dissolved, Total and Bacterial Copper Removal Efficiencies versus Influent Copper Concentration for Reactor IVA

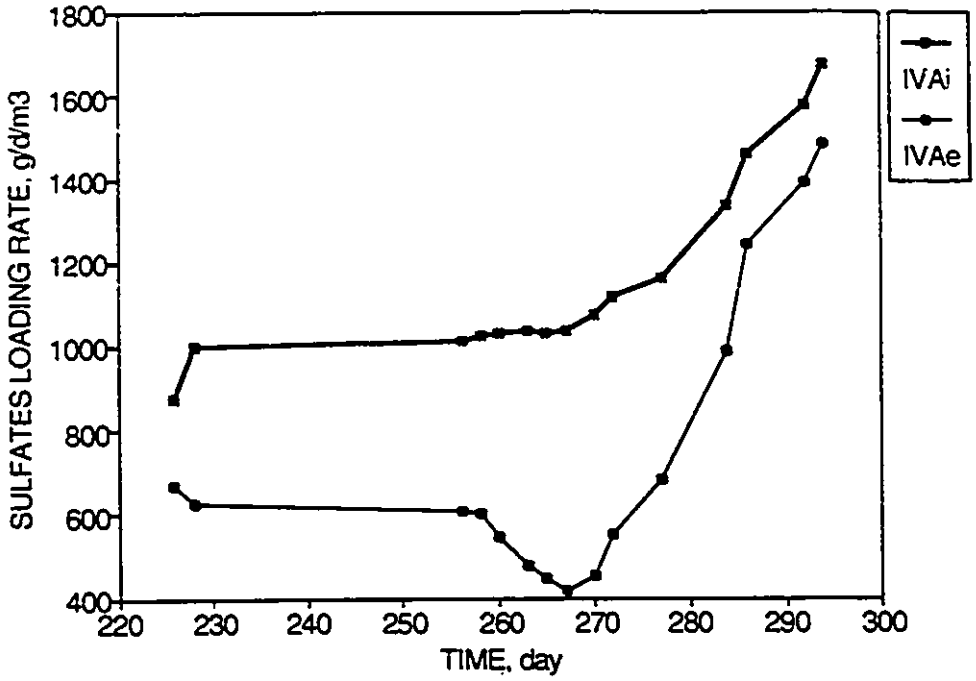


Figure 5.46
Influent and Effluent Sulfate Loading Rates versus Time for Reactor IVA

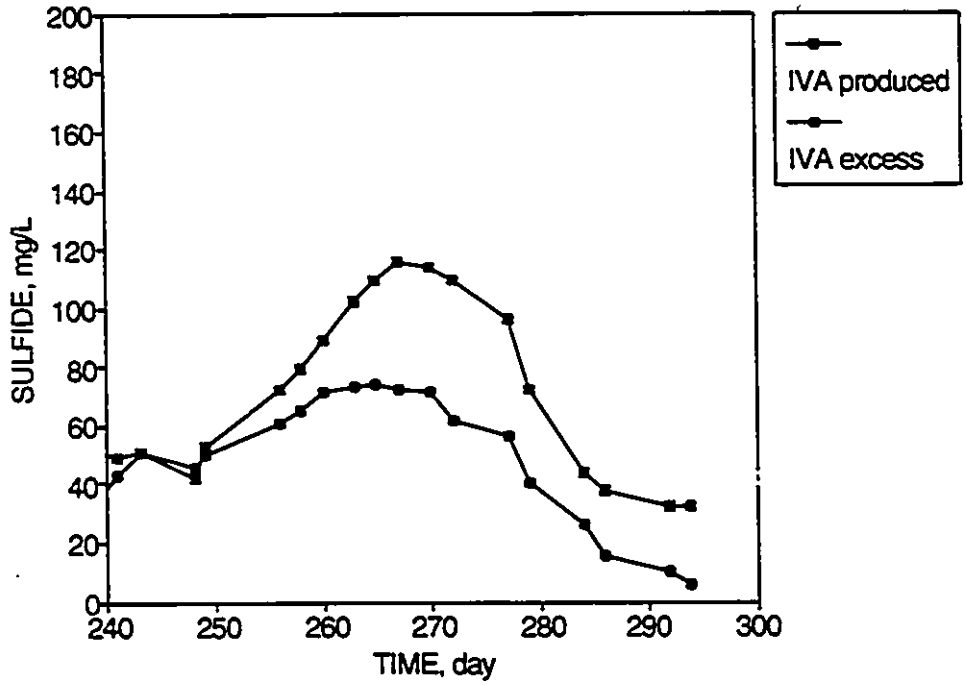


Figure 5.47
Excess Sulfide and Sulfide Produced versus Time for Reactor IVA

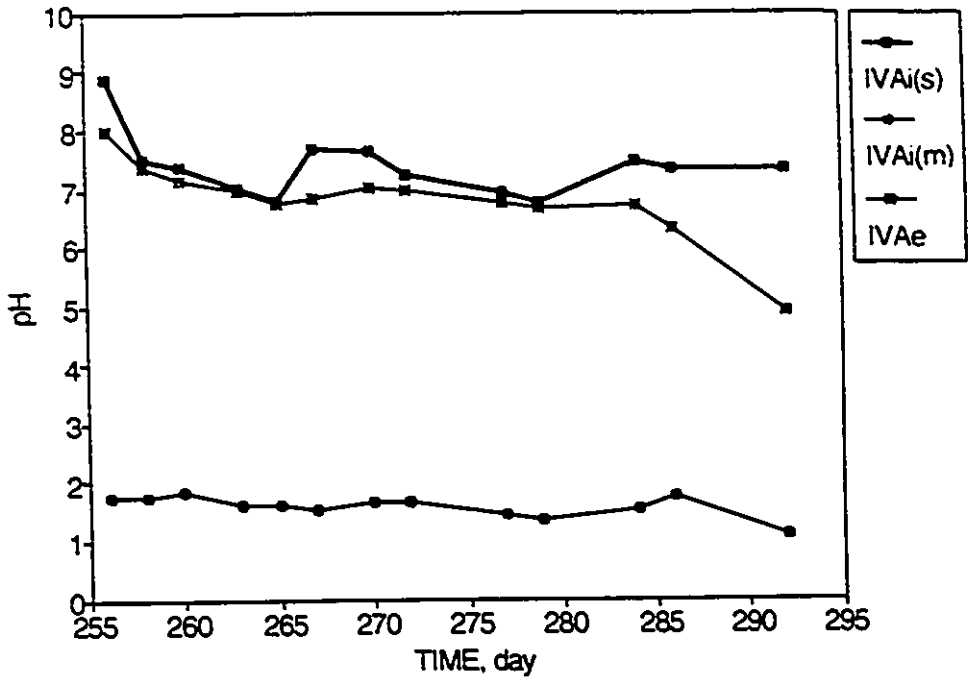


Figure 5.48
Influent (Substrate Line and Metal Line) and Effluent pH Values versus Time for Reactor IVA

The availability of sulfide would not necessarily result in the copper precipitation. Figure 5.47 shows that excess sulfides were available throughout the study. However, the bacterial removal efficiencies were less than or equal to 80%. Therefore, 20% or more of copper was not precipitated as sulfide, eventhough the free sulfide was available. Thus, it supported the previous conclusion that copper sulfide was not the only form of dissolved metal precipitation in the reactor.

5.4.4 Cadmium

The cadmium removal was studied in Reactor IVB. All of the

cadmium in the influent was in soluble form. Figure 5.49 shows the removal in the total and dissolved cadmium. The filter did not remove all of the suspended cadmium, resulting in a higher total effluent concentration as compared to the dissolved concentration.

The cadmium removal, in the Control Reactor IA, is shown in Figure 5.50. They represented the non-bacterial cadmium removals that happened in reactor IVB. Approximately 30% of influent cadmium was removed.

Figure 5.51 depicts that initial acclimation to cadmium occurred before reaching an influent concentration of 100 mg/L. After the acclimation, the bacterial metal removal efficiencies were 80%. The dissolved removal efficiencies were 99% throughout the study. However, the filter could not maintain a satisfactory suspended metal removal at a high influent cadmium concentrations. It was indicated by the decrease in the total removal efficiency with the increase in the cadmium concentration. With 50 mg/L or lower concentration, the total cadmium concentration removal efficiency was 70%. On the other hand, at 230 mg/L concentration, only 20% total removal efficiency was achieved.

The cadmium did not inhibit sulfate reducing bacteria, as is shown by a constant sulfate reduction throughout the study (Figure 5.52). Approximately 600 g/d/m3 was reduced ,which is comparable with the reduction in Reactor IIB. Reactor IIB was intended to monitor the sulfate reduction in the absence of interfering substances, such as dissolved heavy metals. As shown in Figure 5.54, Reactor IVB was able to maintain pH around 7.

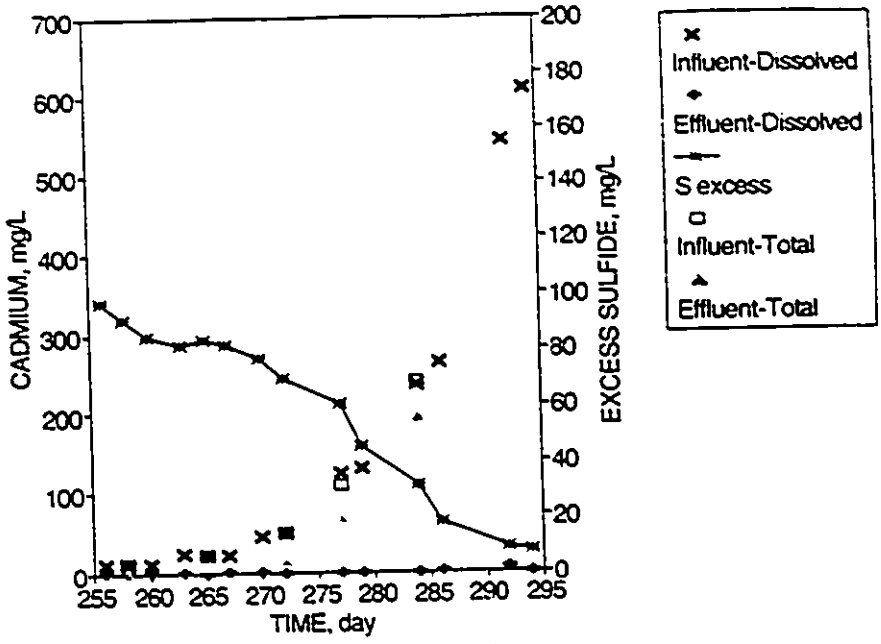


Figure 5.49
Dissolved and Total Cadmium Concentrations and Excess Sulfide versus Time for Reactor IVB

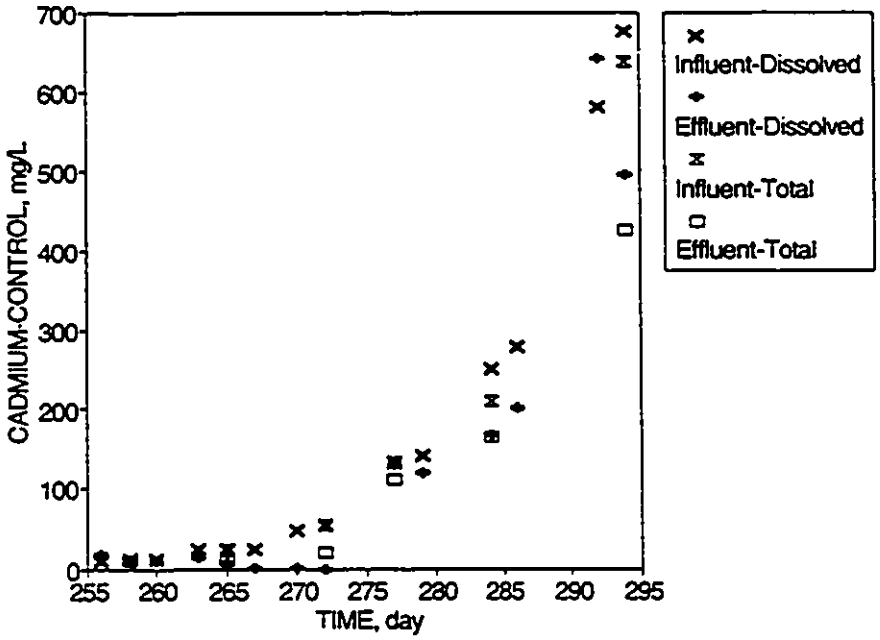


Figure 5.50
Dissolved and Total Cadmium Concentrations versus Time for Reactor IA

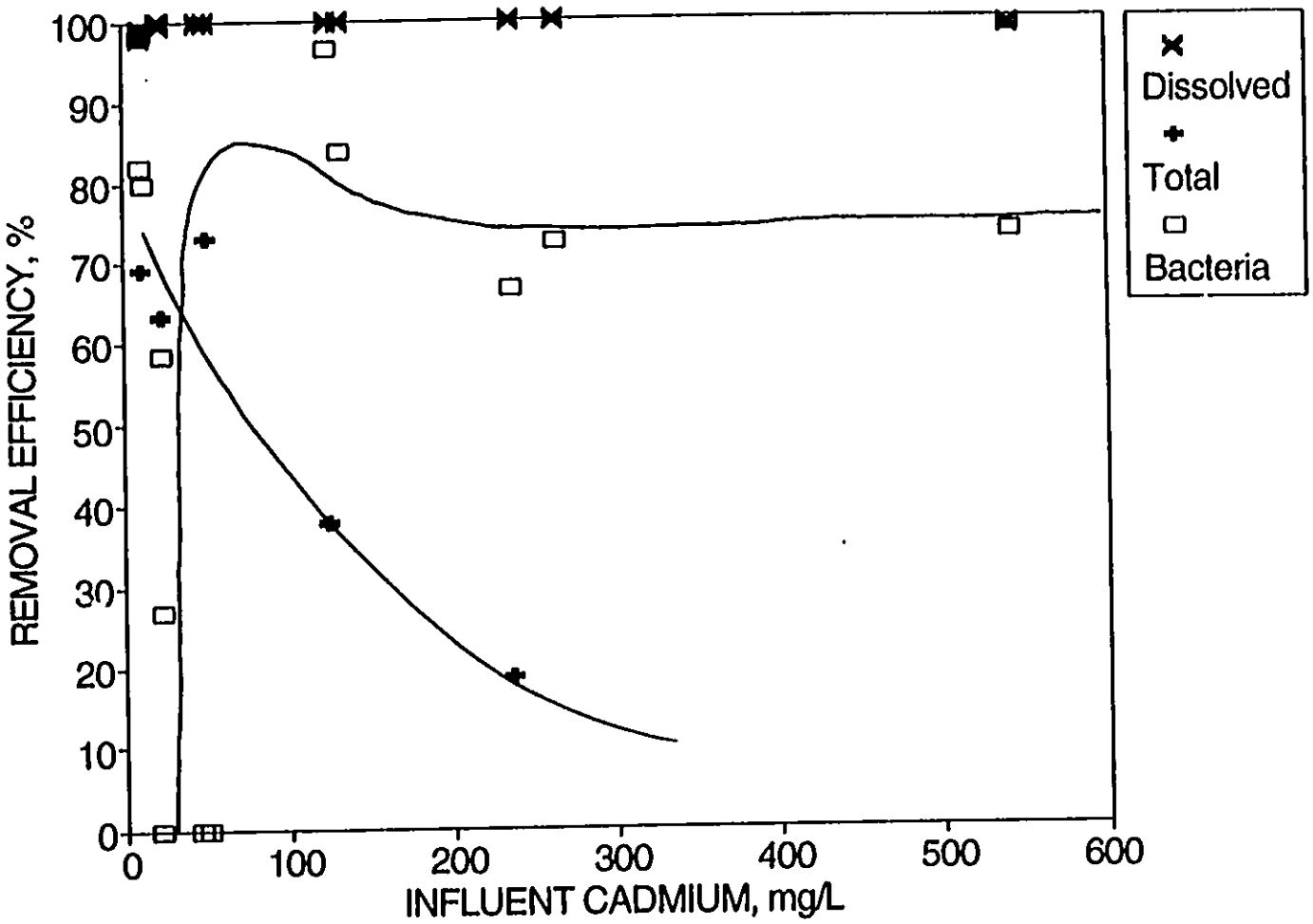


Figure 5.51
Dissolved, Total and Bacterial Cadmium Removal Efficiencies versus Influent Cadmium Concentration for Reactor IVB

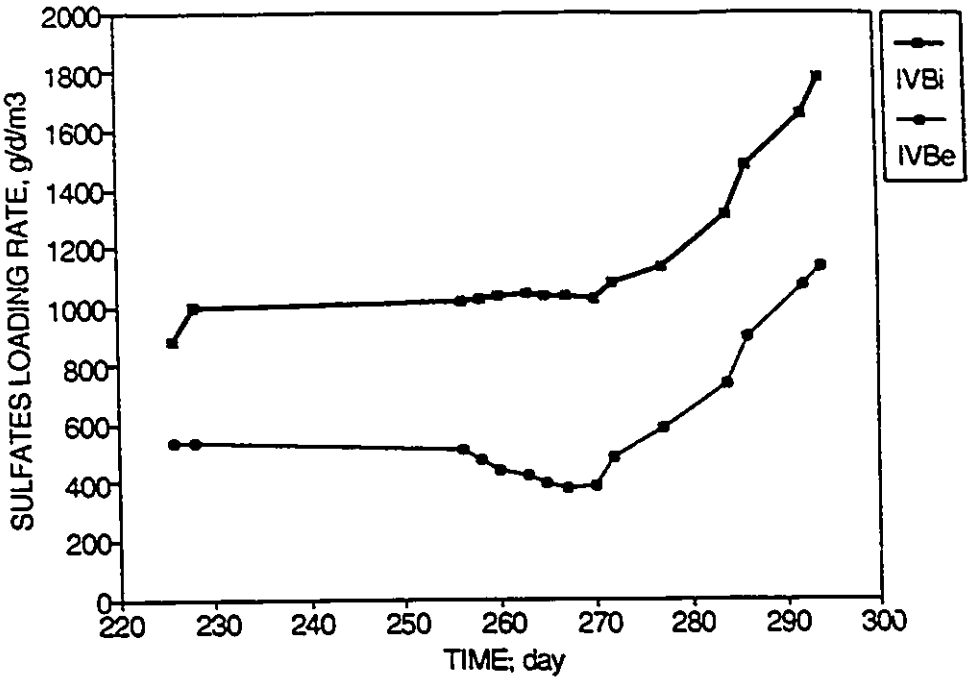


Figure 5.52
Influent and Effluent Sulfate Loading Rates versus Time for Reactor IVB

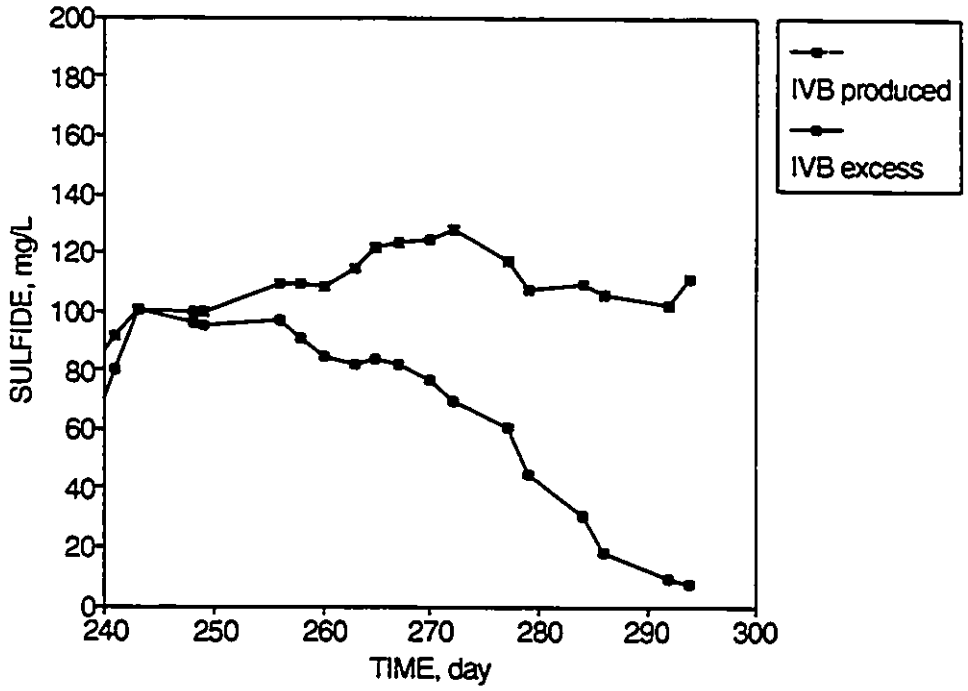


Figure 5.53
Excess Sulfide and Sulfide Produced versus Time for Reactor IVB

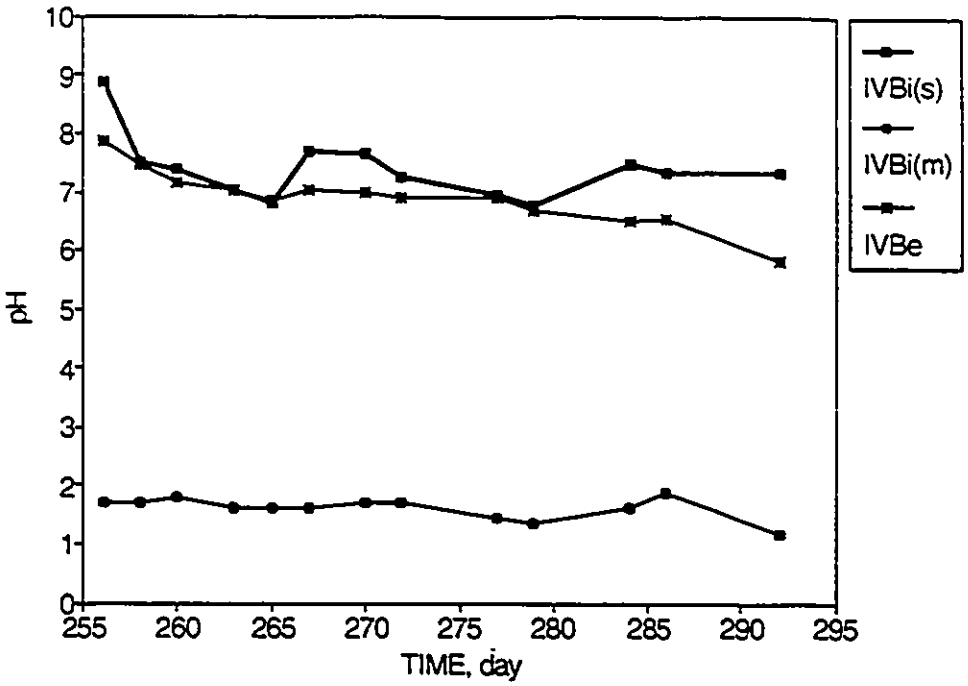


Figure 5.54
Influent (Substrate Line and Metal Line) and Effluent pH Values versus Time for Reactor IVB

Figure 5.53 indicates that there was a decrease in the excess sulfides as more cadmium was precipitated. All the sulfides produced were used up at a chromium concentration of 550 mg/L. Thus, 550 mg/L cadmium was the highest concentration that could be treated by the sulfate reducing bacteria (SRB).

Copper and cadmium had a much higher bacterial removal efficiency when compared with chromium removal efficiency. This resulted because copper and cadmium sulfide had a very low solubility product, as shown in Table 1.2.

5.5 Stoichiometric Analysis

Sulfate reducing bacteria (SRB) reduce sulfates into sulfides and intermediate compounds as shown in Figure 5.5. In this study, it was assumed that all of the sulfates reduced would be converted to sulfides. Using the average results from the metal loading studies, the sulfur balance was carried out. The sulfur balance involved the following steps:

- calculating of the theoretical sulfide production from sulfate reduction;
- measuring the excess soluble sulfide in the effluent;
- calculating theoretical sulfide removal from the difference between the theoretical sulfide production and the excess soluble sulfide measurement;
- computing the theoretical sulfide concentrations needed for the metal precipitation based on metal removed.

Table 5.8 summarized the results of the sulfur balance carried out in this study.

The sulfur balance indicates that the theoretical sulfide removal values are generally higher than the calculated amount needed to precipitate the metals, except in Reactor IVA. The discrepancy was caused by:

- the assumption that the percentage of metal removals in the Control Reactor, IA, represented the non-bacterial metal removals;
- the presence of other metals which were not monitored and formed metal sulfides;

- oversimplification of the metal sulfide reaction:

  $$S + M \text{ ---> } MS$$

- and the assumption that all reduced sulfates would be converted into sulfides.

The detailed sulfur balance calculations are shown in Appendix IV.

Table 5.8
Sulfur Balance

Reactor	Average Sulfate Reduced, mg/L	Theoretical Sulfide Produced mg/L	Average Excess Sulfide in Effluent mg/L	Theoretical Sulfide Removal mg/L	Average Sulfide for Metal Precipitation mg/L
IIIA	304	101	65	36.7	0.94
IIIB	193	60	32	30.2	9.74
IVA	238	79	51	29.6	30.1
IVB	338	113	58	55	32.8

5.6 Oxidation Reduction Potential (ORP)

The measurement of effluent redox potential (ORP), in the metal loading study, indicated the residual sulfide present. On the other hand, in the organic loading and phosphate addition studies, it would monitor whether the reactor was operating within the specified ORP range. The ORP effluent measurement in the metal loading study did not reflect its operating condition. This was because sulfides, the reduction product, would precipitate as metal

sulfides and remain in the reactor. Thus, the effluent would contain only the excess sulfides, not the total sulfides.

Oxidation reduction potentials (ORP) values were measured in the effluent and a correlation between excess soluble sulfide and ORP was established. The correlation was possible because ORP measured the oxidation reduction strength of the solution and sulfide was the reducing agent. A reducing agent is defined as a substance capable of liberating an electron. Figure 5.55 shows the effluent ORP readings versus the corresponding sulfide concentrations. A semi-ln correlation of the following form was used to determine the best fit between the two parameters:

$$ORP = m * Ln\ [S] + b \qquad (5.15)$$

where:

ORP = redox potential (mV)
m = constant (mV * L/mg)
S = excess soluble sulfide, mg/L
b = constant (mV)

Curve fitting the data in Figure 5.55, performed with least squares technique, produced equation 5.16 with R-squared=0.564.

$$ORP = -90.2\ Ln\ [S] + 293 \qquad (5.16)$$

The spread of the data indicates that some other factors also influenced the ORP of the effluent. Lappan (1987) summarized these factors as:

- the presence of other constituents which were in a reduced state, thus contributing to the redox potential of the solution;
- the error associated with the ORP measurement (Appendix III).

Therefore, ORP measurement could be used not only to indicate the oxidation reduction strength of the solution but also to calculate the quantity of the excess soluble sulfides available to precipitate heavy metals.

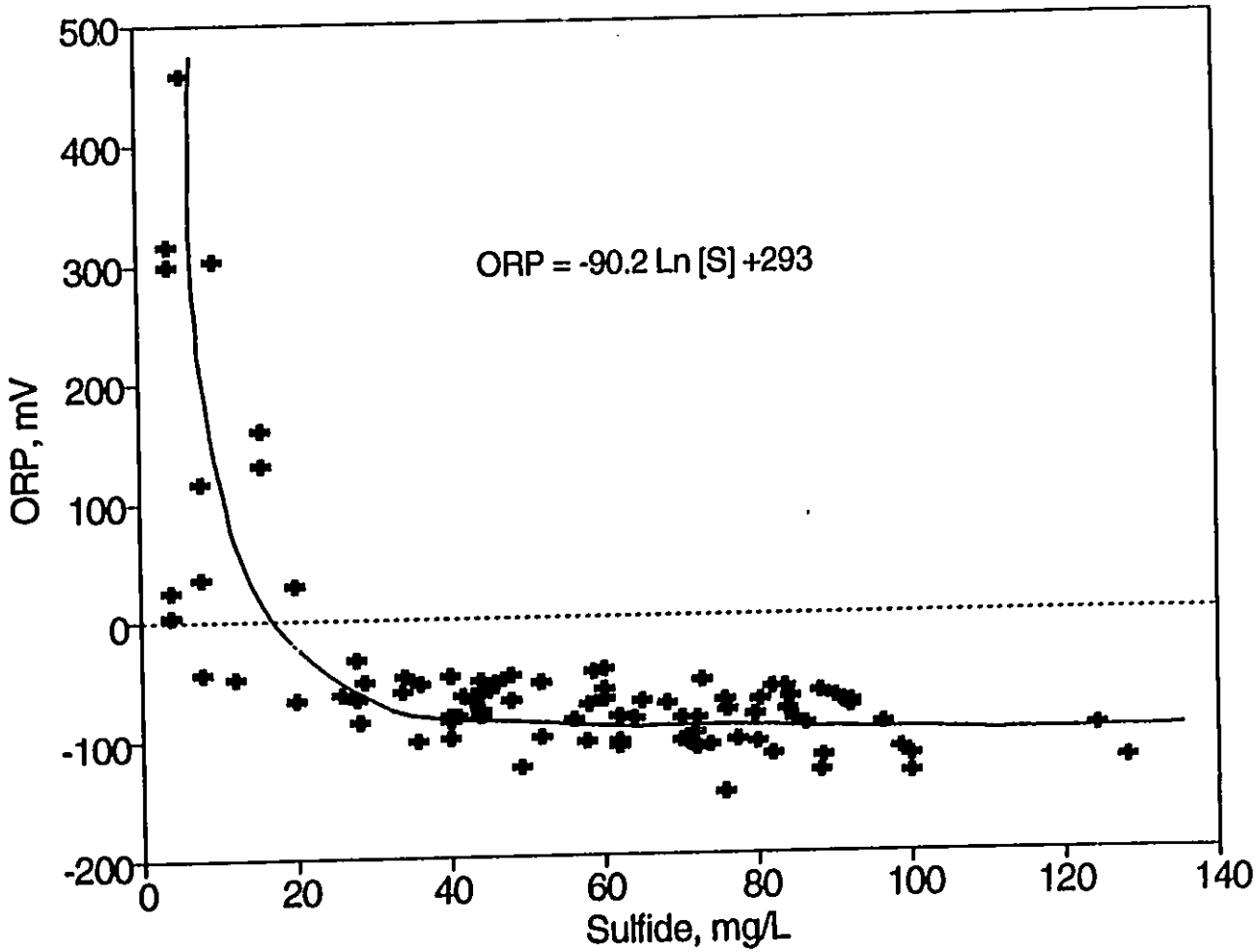


Figure 5.55
ORP versus Excess Sulfide

VI CONCLUSION AND RECOMMENDATION

6.1 Preliminary Studies

The initial studies provided the information on the importance of organic loading and phosphorus requirement to the SRB's performance.

6.1.1 Lactate was used as the organic source. It was found that the sulfide production rate increased with the lactate loading rate until a maximum rate was achieved. After the maximum rate was reached, further addition of lactate did not increase the rate. The optimum sulfide production was achieved at lactate loading of 2 kg/d/m3 ,without phosphate addition, and 6 kg/d/m3 ,with phosphate addition.

6.1.2 With phosphate addition of 0.18 g/L, the anaerobic filters were able to increase the sulfide production rate three to four times higher than the one without addition. The average sulfide production rate had increased from 66 g/d/m3 to 248 g/d/m3. The average number of active bacteria had also increased from 10^6 to 10^8.

6.1.3 Thus, specific attention should be given to not only the organic requirements of the microorganisms, but also to their nutrient requirements if optimum performance is to be achieved.

6.1.4 With 0.18 g/L phosphate addition, the overall average consumptive ratio of the anaerobic filter was 1.2. A value higher than one indicates that some organic oxidation was required for bacterial synthesis. About 17% of the organic matter was used for cell synthesis and the other 83% contributed to sulfate reduction and deoxygenation.

6.1.5 The material balance shows that the lactate requirement and sulfide production can be estimated using the appropriate half reactions from Table 5.2.

6.2 Metal Loading

6.2.1 The dissolved lead, with concentration up to 18 mg/L, could be precipitated with 90% or greater efficiency. However, only 60% to 70% of the total metal was removed. Since most of the dissolved lead was precipitated, it did not inhibit the SRB growth.

6.2.2 The filter was able to remove up to 45 mg/L dissolved chromium with 80% or greater efficiency. All of the precipitated chromium was removed by the filter. Therefore, same removal efficiencies were observed both for the total and dissolved concentrations. The bacterial chromium removal efficiency was 50% to 60%. The filter started to fail at chromium concentration greater than 45 mg/L when metal started to inhibit the SRB, as shown by the decrease in the sulfate reduction. A substantial

decrease in the bacterial chromium removal efficiency was followed by the decrease in the dissolved and total removal efficiencies.

6.2.3 The dissolved and total copper removal efficiencies were 90% or greater throughout the study. All of the precipitated copper was removed. The bacterial removal efficiency was 80% at copper concentration of 60 mg/L. At concentration greater than 60 mg/L, the copper started to inhibit the bacteria, as shown by the decrease in the sulfide production. Regardless of the inhibition, enough sulfide was produced to precipitate 50% of the copper up to 400 mg/L. At 400 mg/L copper, there was no excess sulfide available to treat higher concentration.

6.2.4 The filter was able to remove 99% of the dissolved cadmium. Since almost all of the dissolved concentration was precipitated, the metal did not inhibit the bacteria. Eighty percent of the cadmium was removed by sulfate reducing bacteria (SRB). At 550 mg/L of cadmium, the filter had consumed all of the produced sulfides. Therefore, the maximum cadmium concentration that could be treated by SRB was 550 mg/L. The total cadmium removal efficiency decreased with the increase in the influent metal concentration: 70% at 50 mg/L, 20% at 230 mg/L.

6.2.5 The total metal removal efficiencies varied among the heavy metals: 60%-70% Pb, 20%-70% Cd, 80% Cr, 90% Cu. The order of separation efficiency for the four metals was Cu > Cr > Pb > Cd.

6.2.6 The dissolved metal removal efficiencies were 80% Cr, >90% Pb, >90% Cu, 99% Cd. The maximum metal concentrations that could be treated at those removal efficiencies were: >18 mg/L Pb, 45 mg/L Cr, 400 mg/L Cu and 550 mg/L Cd. The maximum concentration of the lead could not be established, because there was approximately 20 mg/L excess sulfide available to precipitate higher lead concentration. The order of dissolved metal removal efficiency was Cd > Pb, Cu > Cr.

6.2.7 Inhibition to the SRB due to metals was always followed by the decrease in the sulfate reduction and effluent pH. Both parameters can be used as an indicator to the bacterial performance. SRB had the ability to neutralize the reactor pH. The drop in the pH, below neutral value, indicated an upset in the bacterial activity.

6.2.8 The Control Reactor behaviour indicated that sulfide precipitation was not the only way to remove the dissolved heavy metals in the filters. Hydroxide and carbonate precipitation and chelation by organic and inorganic ligands were the other possibilities for dissolved metal removal. Figure 6.1 shows the solubilities of metal hydroxides and sulfides as a function of pH. Metal sulfides have lower solubilities than metal hydroxides. Therefore, sulfide precipitation would occur before hydroxide precipitation in the filters. Both the bacterial and non-bacterial dissolved metal removals occurred in the filters.

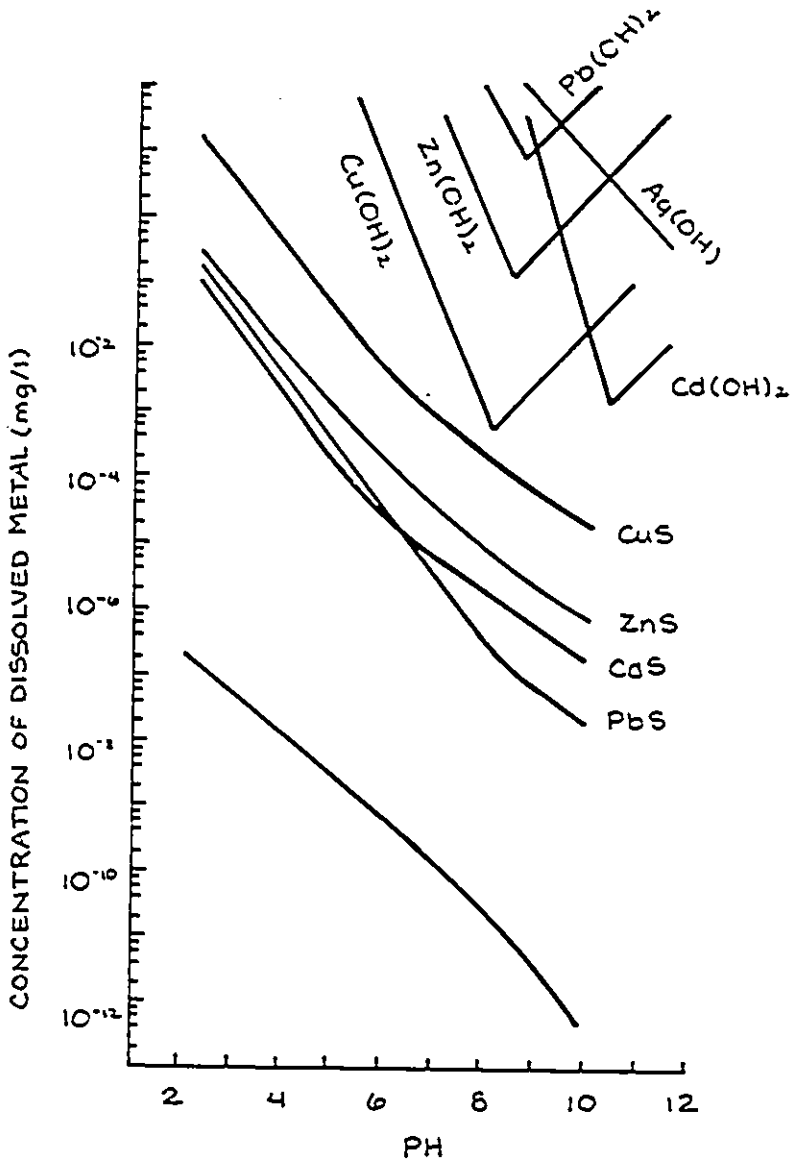


Figure 6.1
Solubilities of Metal Hydroxides and Sulfides as a Function of pH [Cherry, 1982]

6.3 General

6.3.1 The bacterial dissolved metal removal included sulfide and carbonate precipitations because sulfide and carbonate were the product of SRB. The sulfide precipitation was the predominant way in this study. The bacterial metal removal efficiencies were: 80% Cu, 80% Cd, 60% Cr. The bacterial removal efficiency for lead could not be determined, due to the incompatibility of the Control Reactor to Reactor IIIA. The maximum concentrations of heavy metals, that would not inhibit the SRB and be removed with the above bacterial efficiencies, were: 45 mg/L Cr, 60 mg/L Cu, 550 mg/L Cd. Cadmium was the least toxic to the bacteria, whereas copper was the most toxic to the microorganism.

6.3.2 An anaerobic filter is a very effective method for treating a wastewater containing high concentrations of copper and cadmium, up to 400 mg/L and 500 mg/L respectively. However, it is not effective in removing high chromium concentration because chromium preferred hydroxide than sulfide precipitation.

6.4 Recommendations

6.4.1 The application of an anaerobic filter using SRB would require the identification of the type of heavy metals to be treated. It was found that copper and cadmium, at high concentrations, can be treated effectively with this method. A high concentration of chromium would not be recommended for treatment by

this method. Further research is required to study the lead removal, since, in this study, its maximum removal concentration was not achieved. It was also important to study the removal efficiency of the combined heavy metals. It was more common to find a combination of metals in the industrial wastewater.

6.4.2 A representative control reactor was necessary for each phase of the proposed study. The representative control should be designed to simulate the reactor's conditions as closely as possible. It would give a better understanding to the role of sulfate reducing bacteria in the heavy metal removals.

6.4.3 The use of a suitable wastewater, that could be mixed with the metal wastewater, to provide the necessary organic and nutrient requirements for the bacteria is essential. This would eliminate the cost of adding expensive chemicals to supplement the metal wastewater. Domestic wastewater can be a suitable wastewater, because it had a high concentration of organic and nutrient. The mixing ratio between the two wastewaters will have to be established.

6.4.4 Sludge production is another parameter to be considered. The possibility of recirculating sludge should be explored. The excess sludge can be treated to recover the heavy metals for use as soil conditioner and fertilizer. BIOMETEX process, developed by Wong et al. (1985) may be employed.

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APPENDIX I

CALIBRATION AND METHOD OF LLD (LOWER LIMIT OF DETECTION)

I.1 Sulfate

Sulfate was measured using the Turbidimetric method (Standard Method, 1989). Light absorbency of $BaSO_4$ was measured by a photometer. The sulfate concentration was determined by a comparison of the reading with a standard curve. The preparation of the standard curve is explained in the Standard Method (1989). Figure I.1 shows the standard curve obtained in this study.

Two standard curves were prepared. An average of these two curves is plotted and was used in determining the sulfate concentration. The least squares method was used to obtain a straight line for the average curve. The equation of the best fit line with the R-squared value of 0.99 is:

$$SO_4 = 0.247*NTU - 0.918 \qquad (I.1)$$

The minimum detectable concentration [Standard Method, 1989] is approximately 1 ± 0.21 mg SO_4/L. The standard deviation (±0.21) is calculated according to the Standard Method 1030c (1989).

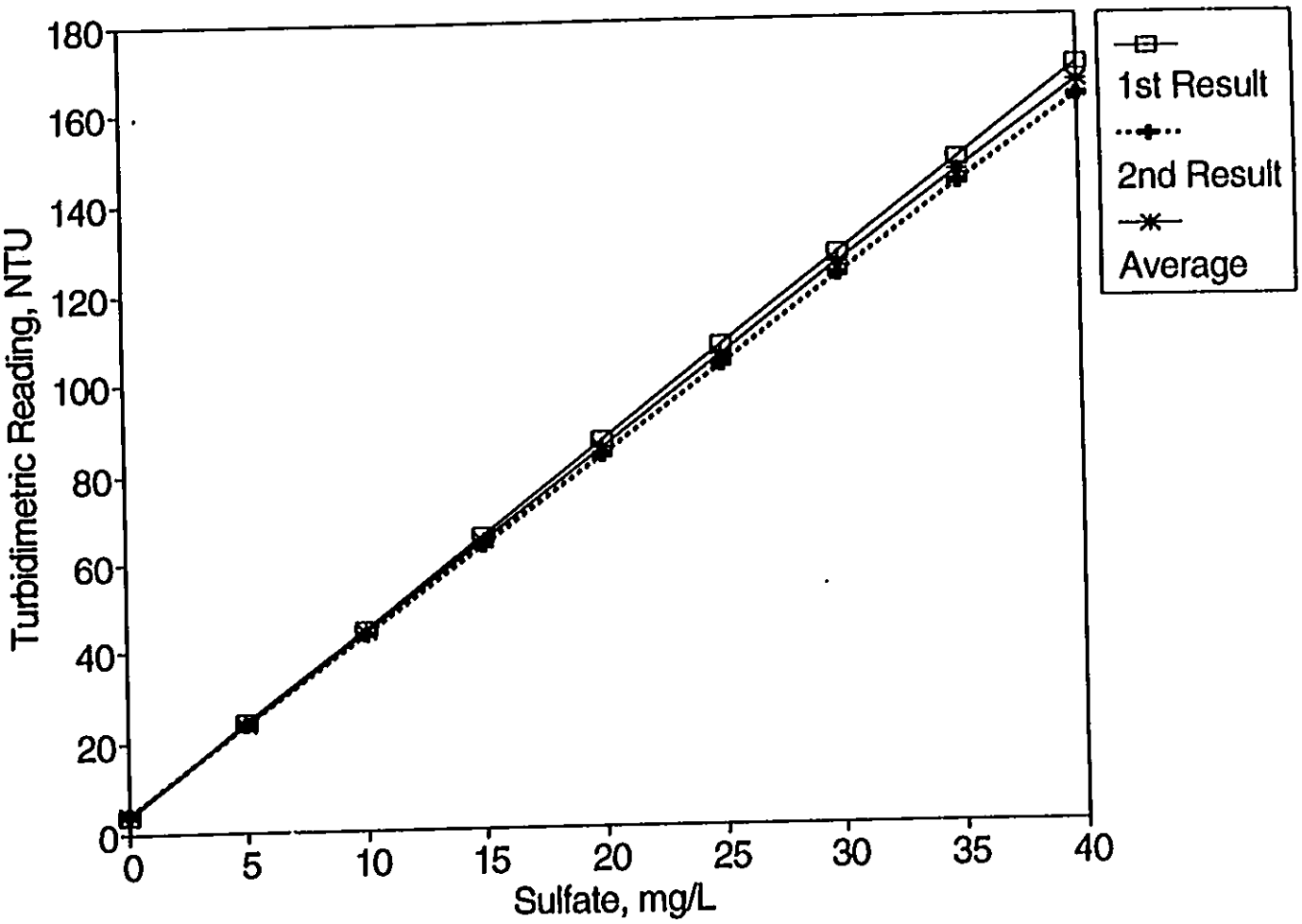

Figure I.1
Standard Curve for Sulfate Determination

I.2 Total Organic Carbon

Total Organic Carbon (TOC) was determined using the persulfate-ultraviolet oxidation method (Standard Method, 1989). The lower analytical limit for which the results can be expressed, also known as Lower Limit of Detection (LLD), was established. According to the Standard Method (1989), LLD is the amount of constituent that produces a signal sufficiently large enough to be detected 99% of the trials.

The LLD value for TOC measurement was developed using the following procedure:

1. Six blank concentrations were measured in the DC-180 TOC analyzer.
2. The average blank concentration and standard deviation were calculated.
3. To reduce the probability of Type I error to 5%, s was multiplied by 1.645 obtained from a cumulative normal distribution table. To further reduce the probability of Type II error to 5%, the above amount was doubled.

The above procedure yielded the LLD of the TOC measurement as:

$$LLD = C_{Blank} + 3.29 * S_{Blank} \qquad (I.2)$$

Where:

C_{Blank} = average concentration of the blank, mg/L; and

S_{Blank} = standard deviation of the blank concentrations, mg/L.

Table I.1
The Results of TOC Measurement in Blank Samples

TOC mg/L	
0.702	Average = 0.591 mg/L
0.637	
0.536	S = 0.0849 mg/L
0.541	
0.651	LLD = 0.87 mg/L
0.479	

The instrument calibration was done by using a high concentration, as specified in the DC-180 Automated TOC operation manual. The instrument performed an automatic linear interpolation as shown in Figure I.2. However, after every five unknown analyses, three known concentration readings were determined to confirm the use of automatic linear interpolation.

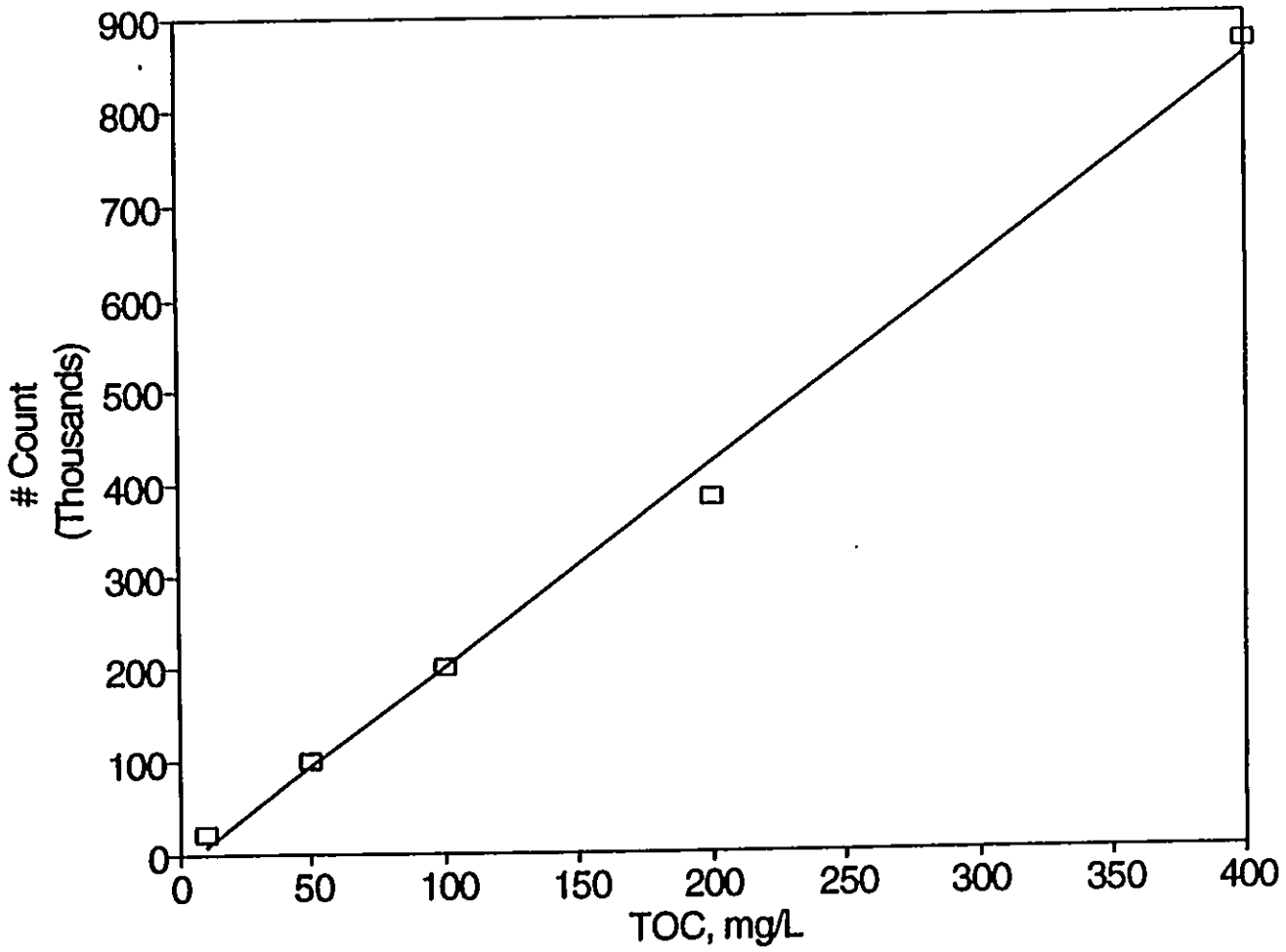

Figure I.2
The Standard Curve for TOC

I.3 Heavy Metals

The metal concentrations were determined using the directly coupled plasma method (Standard Method, 1989). The LLD was determined for each metal, using the following procedure:

1. A set of calibration standards (blank, 0.01, 1, 20, 50, and 200 mg/L) was prepared according to the Standard Method (1989). Three intensity readings were experimentally taker. for each calibration standard.
2. The average intensity for each calibration standard was calculated and plotted. The curve fitting was done using the least squares method. All calibration curves had a correlation of 0.999 or greater.
3. The average blank intensity reading and its standard deviation, for each metal, were calculated.
4. The intensity standard deviation of the blank was multiplied by a factor of three to give a 99.86% confidence level, in determining the presence of the metal (Lappan, 1987).

The following equation for LLD was obtained,

$$I_{LLD} = I_{Blank} + 3*S_{Blank} \qquad (I.3)$$

Where:

I_{LLD} = intensity value of LLD;

I_{Blank} = average intensity value for the blank; and

S_{Blank} = intensity standard deviation for the blank.

Then the calculated I_{LLD} was used to obtain the LLD concentration from the calibration curve. Figures I.3 to I.6 show the calibration curves for different metals. Table I.2 lists the LLD for each ot these metals.

Table I.2
List of LLD for Various Heavy Metals

Metal	I_{LLD}	LLD, mg/L
Pb	163	0.06
Cr	141	0.08
Cu	153	0.07
Cd	159	0.05

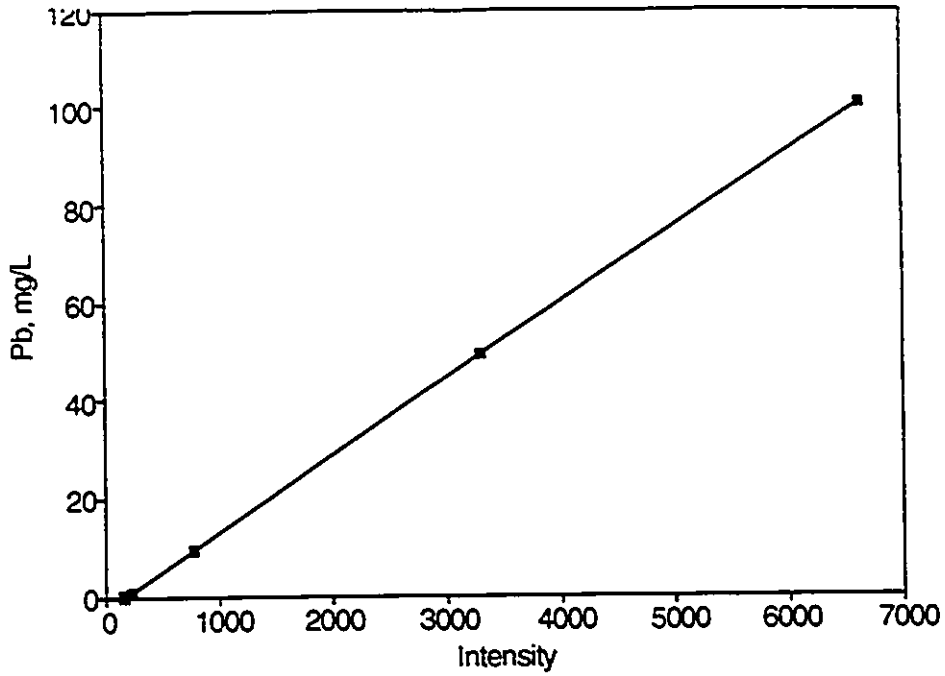

Figure I.3
The Calibration Curve for Lead

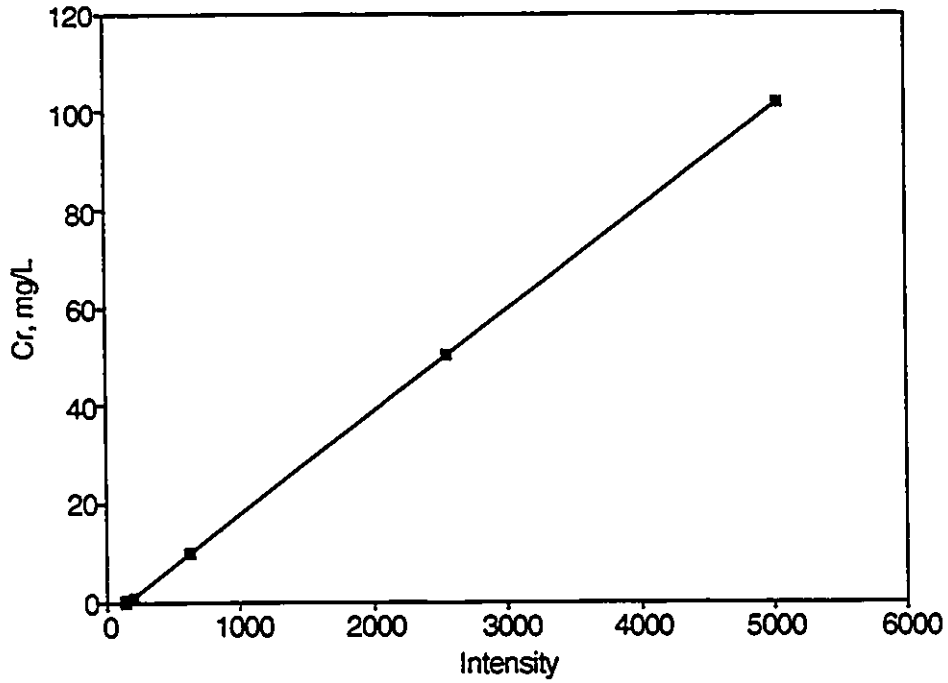

Figure I.4
The Calibration Curve for Chromium

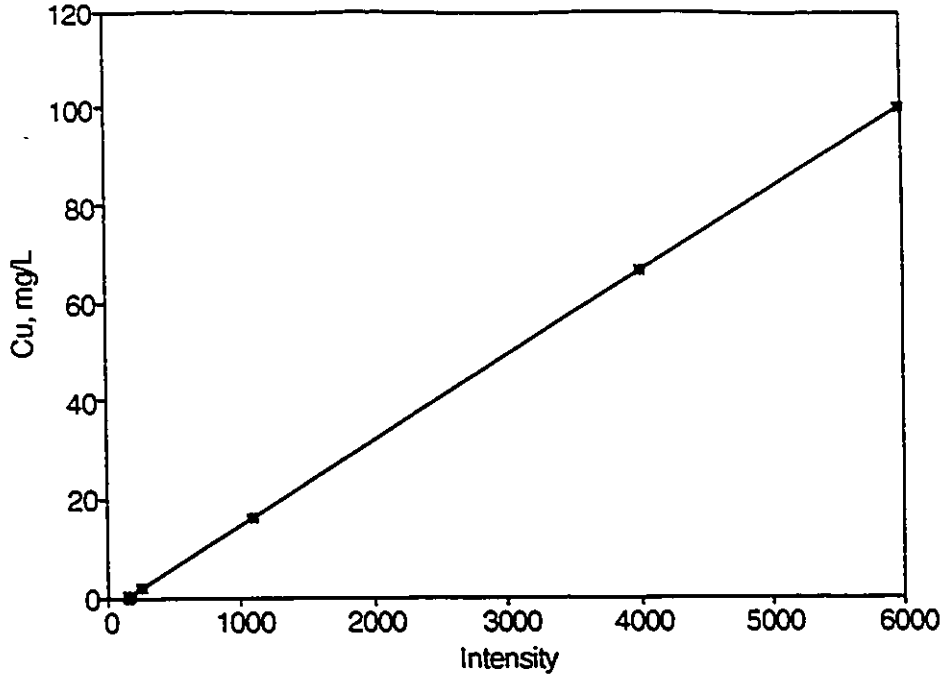

Figure I.5
The Calibration Curve for Copper

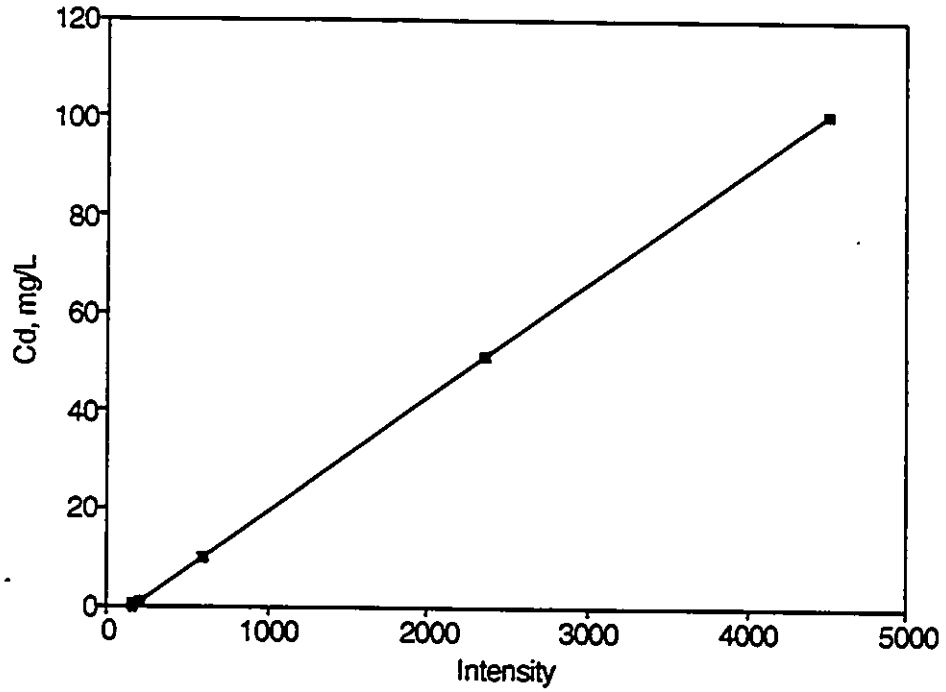

Figure I.6
The Calibration Curve for Cadmium

APPENDIX II

FLOW REGIME

The type of flow in the filter was upflow through packed bed. The hydraulic retention time (HRT) was kept at 12 hours. Lappan (1987) employed the same upflow system in his reactor. He calculated the dispersion numbers of 0.0581 and 0.729 for HRT's of 5.93 and 65.09 hours respectively. These numbers show that the flow regime in the filters, in his study, was plug flow system, with moderate and high dispersion.

A dye test was conducted to investigate the flow regime for this study. Sodium fluorescein was used because it is a good dye solution with density very close to that of water. It was pumped into the reactor. The flow regime was observed by noting the distribution of the orange-yellowish colour of the fluorescein in the reactor. Photographs were taken after 0 hour, 3 hours, 6 hours, 12 hours. The results are shown in Figures II.1 to II.4.

Figure II.1 shows the reactor at time equal to zero, i.e., before fluorescein entered the system. After three hours, the fluorescein had filled approximately a quarter of the reactor, as shown in Figure II.2. Figure II.3 displays the flow after six hours, when almost half of the reactor is filled with the fluorescein. Figure II.4, taken twelve hours after the introduction of the fluorescein, shows that the reactor is completely occupied by the fluorescein.

Obviously, all the particles that entered the reactor stayed in the system for an equal amount of time, i.e., twelve hours. This means flow regime resembled a plug flow system. However, it was not a true plug flow because some dispersion was observed after three

Figure II.1
Dye Test at Zero Hour

Figure II.2
Dye Test After Three Hours

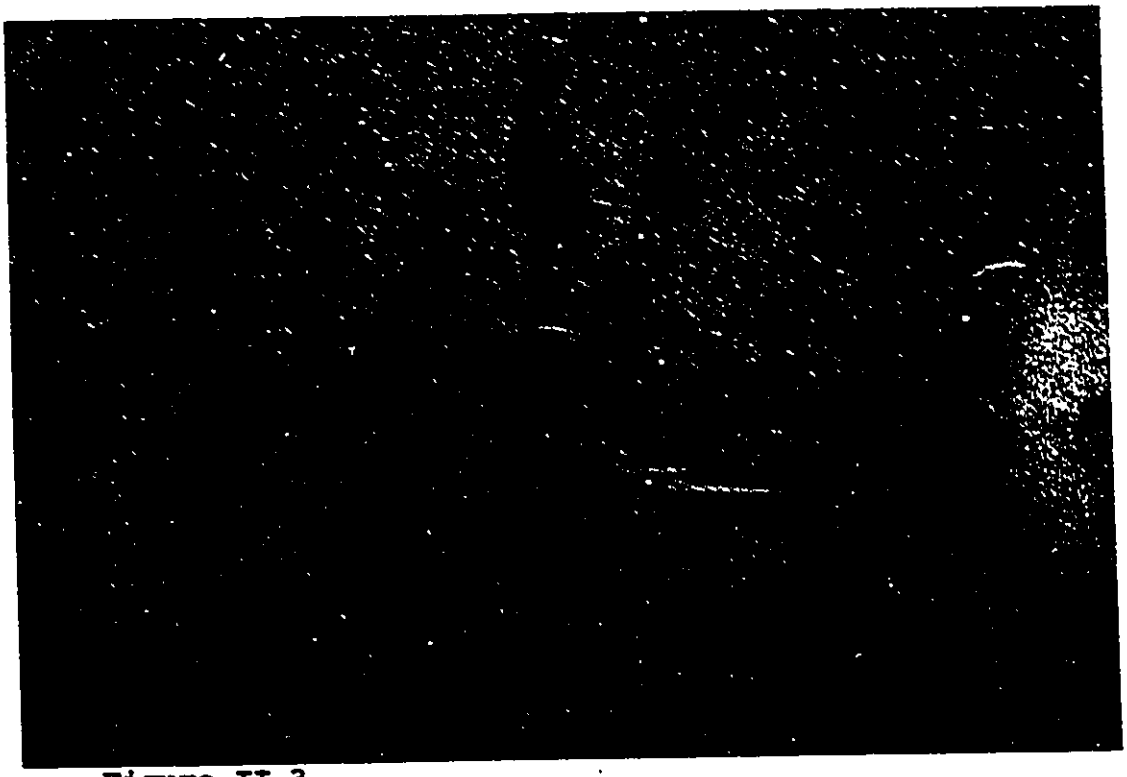

Figure II.3
Dye Test After Six Hours

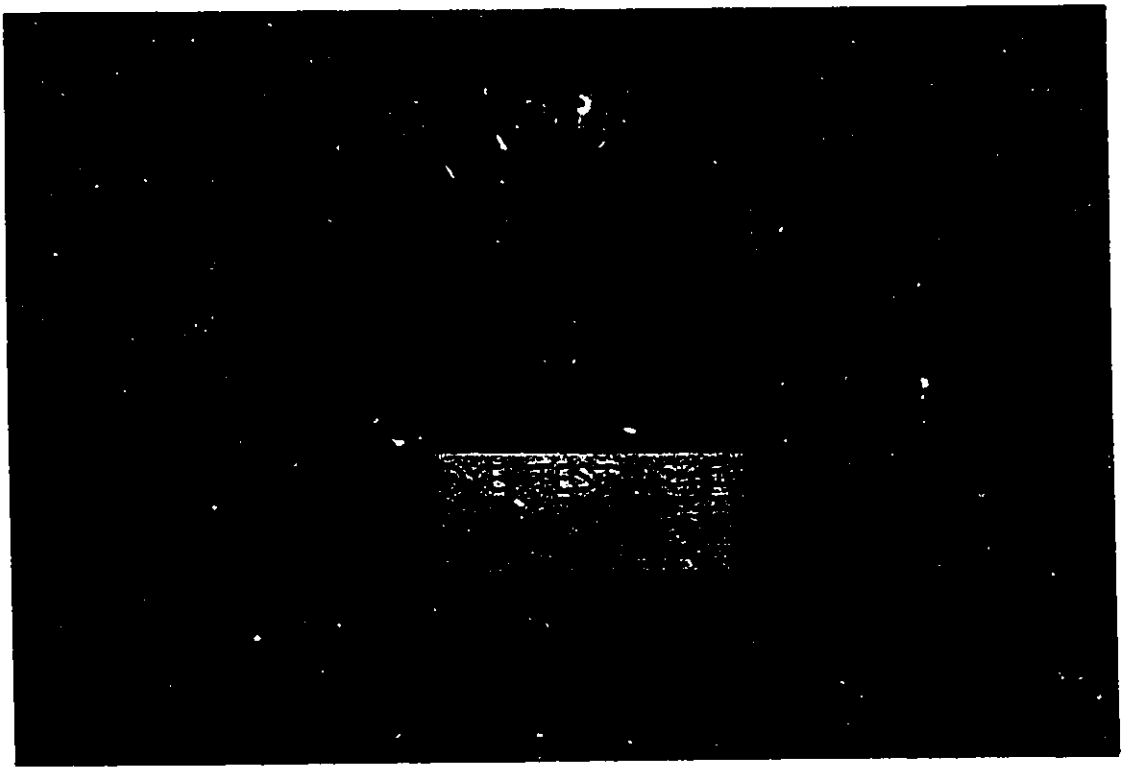

Figure II.4
Dye Test After Twelve Hours

hours, as shown by the light yellow colour of the fluorescein which occupied the whole the reactor (Figure II.2).

Twelve hours of HRT falls between 5.39 and 65.09 hours, the HRT range studied by Lappan (1987). According to Lappan, the flow regime at twelve hours HRT would be a plug flow with a moderate to high dispersion system, as observed in this study. In practice, a true plug flow is difficult to achieve due to longitudinal dispersion (Metcalf and Eddy, 1979).

APPENDIX III

OXIDATION REDUCTION POTENTIAL MEASUREMENT

Oxidation Reduction Potential (ORP) measurement indicates the electron activity of a solution. A solution always contains both reduction and oxidation agents. A reduction agent is defined as a substance capable of liberating electrons. On the other hand, an oxidation agent is defined as a substance capable of accepting electrons. The reduction and oxidation process can be written as follows,

$$\text{Reduction} \rightleftharpoons \text{Oxidation} + e^- \qquad \text{(III.1)}$$

Thus,

$$S^{2-} + 4H_2O \rightleftharpoons SO_4^{2-} + 8H^+ + 8e^- \qquad \text{(III.2)}$$

A redox system is a reduction agent and its corresponding oxidation counterpart.

ORP was measured by immersing a platinum electrode and a reference electrode in the solution to be measured. The platinum potential can be expressed as:

$$e = k + {}^{R*T}/_{F} \ln({}^{a}Ox/{}^{a}Red) \qquad \text{(III.3)}$$

Where:

k = temperature dependent constant;

R = gas constant;

T = temperature in degree Kelvin;

F = Faraday constant;

^{a}Ox = activity of the oxidation agent; and

^{a}Red = activity of the reduction agent.

If the reference electrode is a standard hydrogen electrode, then the potential difference between the platinum and the reference electrodes is:

$$E_h = E^\circ_{Ox\text{-}Red} + {}^{R*T}/_{F} \ln({}^{a}Ox/{}^{a}Red) \qquad (III.4)$$

Where,

$E^\circ_{Ox\text{-}Red}$ = standard potential which is depended on temperature, and the nature of the redox system.

The normal equation for redox potential when hydrogen ions are involved in the chemical reaction is:

$$Red + H_2O \rightleftharpoons Ox + mH^+ + ne^- \qquad (III.5)$$

Then,

$$E_h = E^\circ_{Ox\text{-}Red} + {}^{(R*T)}/_{(n*F)} \ln({}^{a}Ox/{}^{a}Red) - {}^{R*T*M}/_{n}\ pH \qquad ...(III.6)$$

In practice, the standard hydrogen electrode is not suitable as a reference electrode. The most common reference electrode used is calomel electrode. Any measurement performed with the platinum and the calomel electrodes can be converted to yield:

$$E_h = E + E_{reference\ electrode} \qquad (III.7)$$

Where,

E = the measured potential difference between the platinum and the calomel electrodes;

$E_{reference\ electrode}$ = the potential difference between the reference electrodes.

The potential difference between the calomel and the standard hydrogen electrodes is 244.4 mV at 25 °C. Therefore, equation III.7 can be rewritten as:

$$E_h = E + 244.4 \qquad \text{(III.8)}$$

It is difficult to obtain stable ORP measurements in biological fluids. They would tend to shift towards more negative values. The difficulty for obtaining a well-defined redox potential is due to the fact that, frequently, the redox system in the solution slowly exchanges electrons with the platinum electrode (Petersen, 1966).

In order to obtain a stable measurement, Petersen (1966) recommended the addition of a "mediator" to the test solution. A mediator is a redox system capable of making both a rapid and a simple exchange of electrons with the platinum electrode. The requirement for the mediator to function satisfactorily is that the activity (concentration) occurring in its oxidized form should be equal to that in its reduced form.

On the other hand, Lappan (1987) reported no differences in instrumental response rates when the mediators were employed, as suggested by Petersen. As such, Lappan suggested the adoption of a consistent method for redox measurement. Measurements were taken ten minutes after immersing the electrodes in the sample. Lappan

found that the instrument reached at least 95% of the equilibrium reading within ten minutes. Thus, the CRP measurements are underestimated by about 2% (Lappan, 1987).

APPENDIX IV

CALCULATIONS

IV.1 Consumptive Ratio

$$C_R = \frac{\text{Equivalent Decrease in Total Organic Carbon}}{\text{Equivalent Decrease in } SO_4 \text{ and } O_2} \qquad \text{(IV.1.1)}$$

$$\text{Equivalent Decrease in Total Organic Carbon} = \frac{TOC_i - TOC_f}{6^1} \quad \frac{mg/L}{mg/milliequivalent/L} \qquad \text{...(IV.1.2)}$$

$$\text{Equivalent Decrease in } SO_4 = \frac{C_{si} - C_{sf}}{12^1} \quad \frac{mg/L}{mg/milliequivalent/L} \qquad \text{...(IV.1.3)}$$

$$\text{Equivalent Decrease in } O_2 = \frac{DO}{16^1} \quad \frac{mg/L}{mg/milliequivalent/L} \qquad \text{(IV.1.4)}$$

Where,

TOC_i = total organic carbon concentration in influent;

TOC_f = total organic carbon concentration in effluent;

C_{si} = initial SO_4 concentration;

C_{sf} = final SO_4 concentration;

DO = initial dissolved Oxygen concentration.

[1] See Table 5.4

IV.2 Material Balance

Oxidation equation:

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{3}\ H_2O \longrightarrow {}^{1}/_{6}\ CO_2 + {}^{1}/_{12}\ HCO_3^- + H^+ + e^- \quad \ldots(IV.2.1)$$

Reduction equations:

$$^{1}/_{4}\ O_2 + H^+ + e^- \longrightarrow {}^{1}/_{2}\ H_2O \quad (IV.2.2)$$

$$^{1}/_{8}\ SO_4^{--} + H^+ + e^- \longrightarrow {}^{1}/_{2}\ H_2O + {}^{1}/_{8}\ S^{--} \quad (IV.2.3)$$

Cell synthesis:

$$^{5}/_{28}\ CO_2 + {}^{1}/_{28}\ NO_3^- + {}^{29}/_{28}\ H^+ + e^- \longrightarrow {}^{1}/_{28}\ C_5H_7O_2N + {}^{11}/_{28}\ H_2O \quad \ldots(IV.2.4)$$

Sulfate Reduction

Adding equations IV.2.1 and IV.2.3:

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{3}\ H_2O \longrightarrow {}^{1}/_{6}\ CO_2 + {}^{1}/_{12}\ HCO_3^- + H^+ + e^-$$

$$^{1}/_{8}\ SO_4^{--} + H^+ + e^- \longrightarrow {}^{1}/_{2}\ H_2O + {}^{1}/_{8}\ S^{--}$$

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{8}\ SO_4^{--} \longrightarrow {}^{1}/_{6}\ H_2O + {}^{1}/_{8}\ S^{--} + {}^{1}/_{6}\ CO_2 + {}^{1}/_{12}\ HCO_3^- \quad (IV.2.5)$$

Synthesis

Adding equations IV.2.1 and IV.2.4:

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{3}\ H_2O \longrightarrow {}^{1}/_{6}\ CO_2 + {}^{1}/_{12}\ HCO_3^- + H^+ + e^-$$

$$^{5}/_{28}\ CO_2 + {}^{1}/_{28}\ NO_3^- + {}^{23}/_{28}\ H^+ + e^- \longrightarrow {}^{1}/_{28}\ C_5H_7O_2N + {}^{11}/_{14}\ H_2O$$

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{28}\ NO_3^- + 0.01\ CO_2 + 0.036\ H^+ \longrightarrow$$

$$0.06\ H_2O + {}^{1}/_{12}\ HCO_3^- + {}^{1}/_{28}\ C_5H_7O_2N \qquad \text{(IV.2.6)}$$

Deoxygenation

Adding equations IV.2.1 and IV.2.2:

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{3}\ H_2O \longrightarrow {}^{1}/_{6}\ CO_2 + {}^{1}/_{12}\ HCO_3^- + H^+ + e^-$$

$$^{1}/_{4}\ O_2 + H^+ + e^- \longrightarrow {}^{1}/_{2}\ H_2O$$

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{4}\ O_2 \longrightarrow 0.167\ H_2O + {}^{1}/_{6}\ CO_2 + {}^{1}/_{12}\ HCO_3^-$$

...(IV.2.7)

Overall Sulfate Reduction

Adding equations IV.2.5 and IV.2.6:

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{8}\ SO_4^{--} \longrightarrow {}^{1}/_{6}\ H_2O + {}^{1}/_{8}\ S^{--} + {}^{1}/_{6}\ CO_2 + {}^{1}/_{12}\ HCO_3^-$$

$$^{1}/_{12}\ C_3H_5O_3^- + {}^{1}/_{28}\ NO_3^- + 0.01\ CO_2 + 0.036\ H^+ \longrightarrow$$

$$0.06\ H_2O + {}^{1}/_{12}\ HCO_3^- + {}^{1}/_{28}\ C_5H_7O_2N$$

$$0.167\ C_3H_5O_3^- + 0.125\ SO_4^{--} + 0.036\ NO_3^- + 0.036\ H^+ \longrightarrow$$

$$0.227\ H_2O + 0.125\ S^{--} + 0.157\ CO_2 + 0.167\ HCO_3^- +$$

$$0.036\ C_5H_7O_2N \qquad \text{(IV.2.8)}$$

Dividing equation IV.2.8 by 0.125:

$$1.33\ C_3H_5O_3^- + SO_4^{--} + 0.288\ NO_3^- + 0.288\ H^+ \longrightarrow 1.816\ H_2O + S^{--}$$

$$+ 1.256\ CO_2 + 1.33\ HCO_3^- + 0.288\ C_5H_7O_2N$$

Thus,

10 mg/L		12.3 mg/L		3.39 mg/L		3.33 mg/L
Sulfate	+	Lactate	=	Cells	+	Sulfide

Overall Deoxygenation

Adding equations IV.2.6 and V.2.7 yields:

$$^1/_{12}\ C_3H_5O_3^- + {}^1/_{28}\ NO_3^- + 0.01\ CO_2 + 0.036\ H^+ \longrightarrow$$

$$0.06\ H_2O + {}^1/_{12}\ HCO_3^- + {}^1/_{28}\ C_5H_7O_2N$$

$$^1/_{12}\ C_3H_5O_3^- + {}^1/_4\ O_2 \longrightarrow 0.167\ H_2O + {}^1/_6\ CO_2 + {}^1/_{12}\ HCO_3^-$$

$$0.167\ C_3H_5O_3^- + 0.25\ O_2 + 0.0357\ NO_3^- + 0.036\ H^+ \longrightarrow$$

$$0.227\ H_2O + 0.157\ CO_2 + 0.167\ HCO_3^- + 0.0357\ C_5H_7O_2N \quad \text{(IV.2.9)}$$

Dividing equation IV.2.9 by 0.25:

$$0.67\ C_3H_5O_3^- + O_2 + 0.143\ NO_3^- + 0.144\ H^+ \longrightarrow$$

$$0.908\ H_2O + 0.628\ CO_2 + 0.67\ HCO_3^- + 0.14\ C_5H_7O_2N$$

Thus,

10 mg/L		18.6 mg/L		4.94 mg/L
DO	+	Lactate	=	Cells

The quantity of lactate required for sulfate reduction could be obtained from equations IV.2.8 and IV.2.9. The stoichiometric amounts given could be expressed as:

$$C_{lt} = 1.23\ C_{si} + 1.86\ DO \qquad \text{(IV.2.10)}$$

where,

C_{lt} = the theoretical lactate requirement concentration, mg/L;

C_{si} = the initial SO_4 concentration, mg/L;

DO = the initial dissolved Oxygen concentration, mg/L.

$$C_{lm} = (TOC_i - TOC_f) * {}^{89}/_{36} \qquad \text{(IV.2.11)}$$

and C_{lm} is the measured lactate requirement concentration, mg/L.

IV.3 Bacterial Removal Efficiency

In this study, both bacterial and non-bacterial heavy metal removals had occurred. The bacterial heavy metal removal occurred due to precipitation with sulfide, a microbial product. The non-bacterial heavy metal removal was due to hydroxide and carbonate precipitation as well as chelation by organic and inorganic ligands.

This section explains the method to calculate the bacterial heavy metal removal. The assumption is made that the amount of

metals available to precipitate with sulfide will be those that remained after the non-bacterial metal removal from the initial dissolved metal concentration. The metal removal in the Control Reactor is assumed to represent the percentage of heavy metal removal due to non-bacterial activity (hydroxide and carbonate precipitation, chelation with organic and inorganic ligands).

$$R_b = \frac{(M_i - (R_{nb}/100)*M_i) - M_f}{M_i} *100\% \qquad \text{(IV.3.1)}$$

where,

R_b = bacterial heavy metal removal efficiency, %;

R_{nb} = non-bacterial heavy metal removal efficiency (from Control Reactor), %;

M_i = initial dissolved heavy metal concentration, mg/L;

M_f = final dissolved heavy metal concentration, mg/L.

And,

$$R_{nb} = \frac{M_{ci} - M_{cf}}{M_{ci}} *100\% \qquad \text{(IV.3.2)}$$

Where,

M_{ci} = initial dissolved heavy metal concentration in the Control Reactor;

M_{cf} = final dissolved heavy metal concentration in the Control Reactor.

IV.4 Sulfur Balance

Theoretical Sulfide Production (mg/L) = $(C_{s_i} - C_{s_f}) * {}^{32}/_{96}$

.....(IV.4.1)

Where,

C_{s_i} = initial SO_4^{--} concentration, mg/L

C_{s_f} = final SO_4^{--} concentration, mg/L

Theoretical Sulfide Removal (mg/L) =

Theoretical Sulfide Production - Residual Sulfide in Effluent

..... (IV.4.2)

$$\text{Metal Sulfide} = \{(M_i - (R_{nb}/100) * M_i) - M_f\} * {}^{es}/_{em} \qquad \text{(IV.4.3)}$$

where,

es = sulfide, g/equivalent (see Table IV.4.1)

em = metal, g/equivalent (see Table IV.4.1)

Table IV.4.1
Equivalent Sulfide and Metal Concentrations in Metal Sulfide

Metal	**es** g/equivalent	**em** g/equivalent
Cd	16	56.2
Ni	16	29.4
Cu	16	31.8
Cr	48	34.7
Pb	16	103.6

Table IV.4.1 is constructed based on the metal sulfide reactions:

$$CdS \longrightarrow Cd^{++} + S^{--}$$

$$NiS \longrightarrow Ni^{++} + S^{--}$$

$$CuS \longrightarrow Cu^{++} + S^{--}$$

$$Cr_2S_3 \longrightarrow 2\ Cr^{+++} + 3\ S^{--}$$

$$PbS \longrightarrow Pb^{++} + S^{--}$$

APPENDIX V
DATA

V.1 Organic Loading

Table V.1
pH Values (Without Phosphate Addition)

DAY	IAE	IBE	IIAE	IIBE	IIIAE	IIIBE	IVAE	IVBE	Ii	IIi	IIIi	IVi
0	7.76	8.01	7.58	7.74	7.26	7.34	6.9	6.78	7.67	7.67	7.81	7.76
1	7.28	7.87	7.6	7.74	7.17	7.19	7.37	7.4	7.42	7.42	7.49	7.1
8	7.47	7.33	7.02	7.14	7.05	6.97	6.91	6.8	7.62	7.62	7.67	7.71
15	7.32	7.28	7.02	7.04	7.16	6.85	7.07	7.1	7.68	7.68	7.58	7.66
37	7.31	7.27	7.16	7.04	6.97	7.03	7.2	6.94	7.55	7.55	7.7	7.74
44	7.4	7.42	7.18	7.24	7.11	7.24	7.11	7.15	7.51	7.51	8.01	8.18
52	7.58	7.58	7.1	7.46	7.36	7.15	7.52	7.33	7.65	7.65	8.02	8.41
67	6.7	7.4	7.2	7.3	7.1	7.2	7.2	7.2	7.7	7.7	7.9	8
81	7.1	7.5	7.2	7.2	7.1	7.1	7.1	7	7.9	7.9	7.8	7.9
85	7.2	7.6	7.3	7.3	7.1	7.2	7.2	7.2	7.9	7.9	7.9	8.2
99	7.7	7.7	7.3	7.4	7.1	7.2	7.2	7.2	8.1	8.1	7.9	8.3
122	7.7	7.8	7.5	7.6	7.5	7.6	7.4	7.4	8	8	8.1	7.9
129	7.11	7.32	7.02	7.23	7.17	7.13	7.17	7.37	7.49	7.49	7.46	7.78
131	7.32	7.51	7.22	7.29	7.17	7.36	7.28	6.76	7.55	7.55	7.55	7.65
136	7.29	7.29	7.27	7.35	7.16	7.1	7.09	7.18	7.61	7.61	7.59	7.57
162	7.3	7.3	7.3	7.3	7.5	7.2	7.1	7.2	7.6	7.6	7.6	7.8
169	7.3	7.3	7.2	7.2	7.2	7.1	7.1	7.3	7.6	7.6	7.7	7.7
176	7.49	7.49	7.41	7.24	7.19	7.36	7.15	7.27	7.66	7.66	7.72	7.89
179	7.3	7.39	7.25	7.27	7.22	7.31	7.07	7.22	7.68	7.68	7.68	7.71
190	7.42	7.34	7.42	7.3	7.27	7.36	7.14	7.21	7.84	7.84	7.68	7.99
194	7.6	7.45	7.44	7.44	7.35	7.2	7.18	7.34	7.81	7.81	7.79	7.69

Table V.2
Sulfide Concentration and Production Rate (Without Phosphate Addition)

DAY	IIA		IIB		IIIA		IIIB		IVA		IVB	
	mg/L	g/day/m3	mg/L	g/day/m3	mg/L	g/day/m3	mg/L	g/day/m3	mg/L	g/day/m3	mg/L	g/day/m3
16	7.88	11.28	8.69	8.25	12.73	14.01	14.34	20.86	12.73	17.40	13.53	16.69
39	7.27	12.62	9.29	9.85	14.14	18.63	10.91	18.02	16.56	25.78	15.35	22.79
46	8.07	16.18	10.50	12.33	17.76	25.12	11.30	18.56	25.83	41.59	23.00	37.50
54	10.96	22.35	9.34	13.38	16.60	26.53	11.76	20.30	29.52	49.51	25.88	44.53
56	10.15	20.25	11.76	16.69	18.21	28.47	13.78	23.64	29.50	50.06	29.10	50.55
68	9.54	19.09	12.76	18.32	20.02	32.89	13.97	24.39	28.88	52.17	28.47	52.25
78	9.93	19.69	13.96	19.98	20.00	32.75	15.57	27.61	31.28	56.19	29.26	53.97
87	10.34	19.83	15.97	21.82	21.61	34.26	17.99	33.01	32.49	52.69	29.26	52.25
88	8.67	16.10	16.74	22.42	25.63	40.14	20.38	36.34	32.87	52.52	30.87	53.99
94	10.30	18.68	15.96	21.81	27.28	43.53	20.81	36.66	32.50	51.26	29.29	50.62
101	11.53	21.00	15.98	21.49	28.94	45.93	21.65	38.06	34.18	53.51	30.95	52.95
120	13.17	23.51	16.01	21.19	30.20	45.89	22.09	38.13	35.46	56.06	32.63	54.81
123	11.17	20.13	13.20	17.82	27.41	42.27	19.29	34.05	32.28	53.32	26.60	44.62
130	11.77	21.60	11.37	17.10	23.95	38.41	16.64	31.12	32.48	56.24	23.14	40.77
134	11.36	21.65	11.77	18.76	23.54	39.30	17.05	33.07	33.28	59.42	23.54	43.00
137	11.36	21.64	13.79	24.51	21.50	36.91	18.26	35.49	36.11	67.23	24.75	47.33
165	8.52	16.69	13.38	25.83	22.31	42.26	17.44	34.80	33.66	64.43	23.92	47.39
172	8.92	17.70	14.19	28.34	23.52	46.92	18.65	37.23	34.87	69.59	28.38	56.64
178	6.89	13.65	17.02	34.00	27.16	54.20	23.10	46.13	37.70	75.25	32.83	65.54
183	8.10	16.07	18.23	36.43	30.80	61.48	25.93	51.79	41.33	82.53	35.66	71.20
192	7.90	15.66	14.79	29.53	32.21	64.31	24.51	48.94	37.07	74.00	33.83	67.53
197	11.11	22.19	15.97	31.90	33.76	67.42	26.89	53.71	41.04	81.93	36.99	73.86
199	13.91	27.83	16.35	32.40	35.73	71.46	28.87	57.75	43.79	87.59	38.15	75.09
204	15.11	30.23	13.10	25.89	32.04	62.65	24.39	48.77	41.69	83.37	35.25	69.30
206	13.47	26.95	11.45	22.59	27.14	52.85	21.11	42.21	38.78	77.56	33.96	66.72
246	12.44	24.89	13.64	26.97	27.68	53.93	20.46	40.92	40.51	81.02	35.29	69.38
247	10.02	20.04	12.01	23.71	24.03	46.62	17.23	34.45	36.44	72.88	31.23	61.25
261	7.19	14.39	11.99	23.98	20.78	40.13	15.59	31.17	32.77	65.54	28.78	57.55

Table V.3
Sulfate Loading Rate in the Effluent (Without Phosphate Addition)

Day	IAE	IBE	IIAE	IIBE	IIIAE	IIIBE	IVAE	IVBE
	g/day/m3	g/day/m3	g/day/m3	g/day/m3	g/day/m3	g/day/m3	g/day/m3	g/day/m3
15	607.90	706.88	634.64	541.20	533.14	746.55	449.28	564.04
39	742.37	801.78	754.65	580.48	570.09	785.96	471.00	566.05
44	856.99	893.37	886.59	658.40	629.15	792.45	543.76	600.56
52	988.36	977.94	1025.31	708.41	697.78	822.94	602.33	653.39
59	975.05	970.55	971.11	677.19	662.77	779.26	601.71	649.66
67	1012.43	1000.14	962.18	675.04	692.29	761.19	636.00	688.38
81	996.20	985.73	939.76	661.63	691.37	766.83	664.03	722.12
85	974.75	961.44	907.46	622.99	660.41	785.02	598.95	690.51
92	953.20	946.43	866.07	607.34	630.69	754.72	565.50	667.00
99	935.98	938.40	848.81	615.36	645.61	727.92	555.55	661.55
106	901.67	937.48	836.11	607.20	627.08	718.35	541.13	648.20
118	843.42	919.31	819.18	604.84	597.97	708.87	555.08	645.56
122	822.60	968.43	824.90	620.16	613.09	740.69	589.29	658.63
129	840.85	981.27	851.42	702.44	678.95	807.70	654.04	727.60
131	876.92	1008.18	891.05	752.31	704.63	850.85	686.52	760.17
136	883.19	1007.79	895.20	817.98	733.05	855.40	724.17	783.60
162	925.19	1026.13	904.88	875.09	787.42	875.27	746.06	788.65
169	928.40	999.09	926.63	933.95	831.44	879.45	784.61	797.16
176	929.78	1002.25	924.45	924.45	794.82	839.47	752.94	748.47
179	890.54	993.15	892.58	897.53	776.21	813.93	734.14	709.47
190	921.63	1003.84	896.15	902.28	775.42	806.81	726.22	706.51
194	881.33	942.68	834.93	837.56	705.95	731.20	650.22	629.91
199	853.06	878.44	753.35	753.30	620.54	643.90	564.13	542.40
204	781.01		695.76	697.68	556.89	606.69	508.91	503.80
206	753.75		664.29	657.90	512.75	565.92	455.87	461.25
246	691.01		607.08	591.19	453.77	509.70	390.55	398.70
247	687.05		625.89	598.91	476.73	542.56	416.48	429.97

Table V.4
Sulfate Loading Rate in the Influent (Without Phosphate Addition)

Day	IAi	IBi	IIAi	IIBi	IIIAi	IIIBi	IVAi	IVBi
	g/day/m3	g/day/m3	g/day/m3	g/day/m3	g/day/m3	g/day/m3	g/day/m3	g/day/m3
15	598.42	695.35	668.48	552.63	595.43	807.60	535.79	636.11
39	724.34	786.16	783.57	601.07	660.33	870.56	647.50	714.67
44	853.68	888.01	921.79	693.18	723.12	868.51	777.13	802.53
52	981.24	980.31	1052.34	748.50	799.66	900.33	868.07	884.65
59	975.65	975.65	1012.95	730.08	774.11	867.35	868.94	885.52
67	1010.64	1010.64	1010.64	738.63	825.79	878.05	918.52	935.10
81	1003.93	1003.93	1003.93	737.86	828.33	887.25	921.32	944.82
85	980.01	980.01	980.01	706.40	812.50	932.02	846.07	913.19
92	963.02	963.02	963.02	699.06	800.99	920.51	822.85	889.96
99	951.82	951.82	951.82	724.29	828.29	911.45	817.83	884.95
106	914.26	944.22	944.22	710.81	812.00	896.13	809.70	876.81
118	869.30	930.65	930.65	704.64	781.37	887.54	820.09	863.71
122	834.14	951.62	925.94	702.33	789.21	918.95	842.74	865.84
129	850.91	968.39	942.70	777.29	857.03	986.77	899.54	922.64
131	884.75	1002.23	976.54	811.12	881.35	1011.09	925.42	948.52
136	887.17	996.29	970.60	876.06	917.90	1018.81	958.24	981.34
162	921.69	1013.83	973.73	938.63	976.06	1032.24	961.28	984.38
169	931.28	1013.31	998.89	1013.31	1034.46	1034.46	1012.51	1012.51
176	928.51	1010.54	996.12	1010.54	1000.81	1000.81	998.66	998.66
179	882.04	988.77	974.35	988.77	1000.61	1000.61	1000.24	1000.24
190	920.06	1005.19	990.77	1005.19	1007.14	1007.14	1003.41	1003.41
194	864.22	934.93	934.93	934.93	937.08	937.08	952.54	952.54
199	843.26	867.95	867.95	859.42	866.96	866.96	891.90	880.14
204	783.68		808.38	799.84	783.65	810.75	832.92	821.16
206	760.68		760.68	752.14	718.54	745.63	768.59	756.84
246	679.92		679.92	671.39	648.86	675.96	699.32	687.56
247	682.49		682.49	673.96	663.31	690.41	708.03	696.27

Table V.5
Lactate Loading Rate (Without Phosphate Addition)

Day	IAE	IBE	IIAE	IIBE	IIIAE	IIIBE	IVAE	IVBE
	kg/day/m3	kg/day/m3	kg/day/m3	kg/day/m3	kg/day/m3	kg/day/m3	kg/day/m3	kg/day/m3
1	0.398	0.571	0.452	0.492	0.525	0.616	0.296	0.531
8	0.381	0.519	0.336	0.345	0.431	0.605	0.339	0.531
15	0.347	0.515	0.333	0.368	0.456	0.676	0.412	0.453
37	1.301	1.295	1.529	1.142	1.164	1.453	1.662	1.662
44	1.176	1.176	1.425	0.918	0.906	1.381	1.295	1.295
52	1.655	1.655	1.655	1.188	1.404	1.538	1.931	2.114
59	1.538	1.538	1.538	1.205	1.205	0.986	2.114	2.114
67	1.634	1.634	1.634	1.082	1.369	1.369	1.882	1.882
81	1.604	1.604	1.604	1.292	1.292	1.604	2.139	2.139
85	1.878	1.878	1.878	1.299	1.630	1.878	2.174	2.174
92	1.763	1.763	1.763	1.301	1.557	1.763	2.076	2.351
99	1.527	1.527	1.527	1.089	1.235	1.527	1.519	2.035
106	1.632	1.632	1.632	1.115	1.413	1.413	1.884	1.884
118	1.482	1.482	1.482	1.482	1.647	1.647	1.976	1.976
122	1.535	1.800	1.800	1.172	1.705	2.000	2.046	2.046
129	1.322	1.590	1.590	1.206	1.340	1.766	2.120	2.120
131	1.280	1.772	1.547	1.113	1.422	1.969	1.789	2.063
136	1.800	1.800	1.800	1.800	2.000	2.000	2.400	2.400
162	4.000	4.000	4.000	4.000	4.000	4.000	4.800	4.800
169	3.562	4.000	4.000	4.000	4.000	4.000	4.800	4.800
176	3.717	4.000	3.717	4.000	4.000	4.000	4.800	4.800
179	3.055	3.959	3.959	3.959	3.959	3.959	4.751	4.751
190	8.000	8.000	8.000	8.000	8.000	8.000	9.600	9.600
194	6.950	8.000	8.000	8.000	8.000	8.000	9.600	9.600
199	8.000	8.000	8.000	8.000	8.000	8.000	9.600	9.600
204	8.000	8.000	8.000	8.000	8.000	8.000	9.600	9.600
206	8.000	8.000	8.000	7.493	8.000	8.000	9.600	8.802
246	8.000		8.000	8.000	6.405	8.000	9.600	9.600
247	8.000		8.000	8.000	8.000	8.000	9.600	9.600

V.2 Phosphate Addition

Table V.6
pH Values (With Phosphate Addition)

DAY	IAE	IIBE	IIIAE	IIIBE	IVAE	IVBE	I	II	III	IV
1	7.47	7.04	6.78	6.81	6.77	6.83	7.57	7.57	6.99	7
8	7.24	7.17	6.96	7.02	7.14	69	7.23	7.23	7.12	7.17
10	7.05	69	6.56	6.76	6.57	6.61	7.53	7.53	7.19	7.2
13	7.13	7.11	6.71	6.85	6.42	6.47	7.01	7.01	6.93	6.94
15	6.98	6.91	6.56	6.67	6.33	6.46	7.41	7.41	7.07	68
20	7.02	6.87	6.73	6.82	6.67	6.53	6.96	6.96	6.83	6.85
22	7.11	6.92	6.75	68	6.63	6.47	73	73	7.04	6.92
34	7.75	7.48	7.16	7.45	7.22	7.11	8.07	8.07	8.01	7.88
35	7.81	7.44	6.94	7.37	7.25	7.12	7.92	7.92	7.83	7.75
41	7.71	7.34	6.93	7.34	7.07	7.19	8.07	8.07	7.95	7.94
47	7.65	7.43	7.17	7.43	6.86	7.07	7.93	7.93	7.82	7.54
50	6.89	6.72	6.59	6.59	68	6.98	7.08	7.08	7.54	7.47
52	7.17	6.93	6.65	6.56	6.61	6.86	7.51	7.51	7.45	7.41
54	7.41	7.23	6.94	7.37	6.78	6.91	7.73	7.73	7.47	7.42
55	6.35	6.65	6.49	6.68	6.55	6.62	6.28	6.28	6.39	6.35
56	6.38	6.66	6.51	6.66	6.54	6.7	6.45	6.45	6.44	6.45
57	6.52	6.76	6.75	6.66	6.56	6.63	6.56	6.56	6.52	6.42
62	6.57	6.76	6.94	6.96	6.93	6.95	6.92	6.92	7.14	7.12
63	6.61	6.66	6.88	7	6.89	69	7.02	7.02	7.36	7.26
64	6.56	6.61	6.68	6.82	6.75	6.82	6.65	6.65	67	6.78
69	6.68	6.79	6.97	7.07	6.99	71	7.06	7.06	7.31	7.31
70	6.57	6.76	6.71	6.79	6.84	6.87	65	65	6.54	6.64
72	6.62	7.15	6.79	69	6.96	7.05	6.93	6.93	6.96	7.35
73	6.45	6.73	6.65	6.78	6.57	6.72	6.71	6.71	6.79	63
75	6.86	6.85	6.87	7.12	6.73	6.88	6.96	6.96	7.07	6.83
77	6.8	7	71	7	7	71	7	7	7	71
78	6.83	7.15	7.11	7.16	7.11	7.24	7.17	7.17	7.21	7.29
79	6.79	7.14	7.12	7.03	7.11	7.25	7.23	7.23	72	7.25
81	6.73	7.09	7.09	6.94	7.21	7.24	7.15	7.15	7.12	7.37
83	6.68	7	6.98	6.94	7.19	7.1	69	69	6.94	7.05
84	6.66	6.94	7.01	6.84	7.25	7.02	6.85	6.85	69	69
85	6.59	6.91	6.88	6.88	6.96	7.06	6.79	6.79	6.83	6.82
91	6.92	7.15	6.99	6.95	7.02	7.07	7.14	7.14	7.08	6.93
92	67	7.05	6.96	7.01	7.02	7.04	7.09	7.09	7.08	6.96
96	6.58	7.26	7.07	7.01	7.05	7.39	6.91	6.91	7.01	6.93
97	6.37	6.86	6.84	6.81	6.86	7.09	6.73	6.73	6.85	6.73
98	6.51	7.05	6.99	6.96	7.04	7.26	6.88	6.88	7	6.84
99	6.36	6.96	6.84	6.86	6.86	7.15	6.89	6.89	6.92	6.93
100	6.31	6.85	6.83	6.81	6.86	7.07	6.87	6.87	6.77	6.88
103	6.36	68	6.86	6.78	6.77	6.87	68	68	68	6.74
105	6.45	6.91	6.69	6.83	6.6	7.01	6.72	6.72	6.78	6.74
106	6.44	6.89	6.73	6.86	6.85	7.05	68	68	6.74	6.72
107	6.5	7.02	6.84	6.85	6.95	6.98	6.96	6.96	6.84	69
110	6.42	7.06	6.79	6.97	7	7	6.96	6.96	6.81	6.83
113	6.46	6.93	6.79	6.99	6.99	7.04	6.94	6.94	6.82	69
114	6.59	7.05	6.96	7.08	7.09	7.13	6.94	6.94	6.84	7.03
118	6.38	6.98	6.89	6.95	6.83	7.08	7.12	7.12	6.83	7.06
119	6.55	7.03	6.93	69	6.93	7.18	72	72	6.89	7.07
121	6.42	7.04	7.05	6.99	6.89	6.98	7.28	7.28	6.85	6.84
124	6.29	7.18	7.35	7.15	7	7	6.89	6.89	6.82	6.84
154	6.89	7.23	7	7.11	7.01	7.15	7.16	7.16	7.05	7.23
158	6.61	6.96	7.01	6.89	6.83	6.95	6.85	6.85	6.76	6.72
161	6.67	7.14	7.14	7.04	7.13	7.46	7.07	7.07	7.03	7.18
165	6.29	6.98	7	6.87	6.76	7.43	6.74	6.74	6.96	6.74

Table V.7
Sulfide Concentration and Production Rate (With Phosphate Addition)

DAY	IAE		IIBE		IIIAE		IIIBE		IVAE		IVBE	
	mg/L	g/Day/m3	mg/L	g/Day/m3	mg/L	g/Day/m3	mg/L	g/Day/m3	mg/L	g/Day/m3	mg/L	g/Day/m3
52	2.78096	4.742144	17.48032	34.96064	21.45312	42.90624	17.8776	35.7552	12.71296	25.42592	8.74016	14.17233
54	3.17824	5.619307	25.42592	50.85184	28.20688	56.41376	23.43952	46.87904	17.8776	35.00806	12.71296	20.56446
55	2.58232	4.916832	31.58376	63.16752	31.58376	63.16752	25.62456	51.24912	23.63816	45.73697	16.8844	27.17508
56	2.58232	5.16464	33.17288	66.34576	32.37832	64.75664	27.21368	54.42736	26.02184	50.50433	20.8572	33.68491
57	1.78776	3.57552	39.26008	76.30046	36.08184	72.16368	31.69896	63.39792	29.69976	57.86017	24.52232	38.2093
64	2.9988	5.9976	41.39368	80.56766	39.80456	79.60912	33.80696	67.61392	28.56552	54.86302	27.80296	42.57096
70	2.80656	5.61312	41.34224	80.46478	40.53488	81.06976	34.91536	69.83072	31.69232	60.22373	32.1216	48.6642
72	2.21064	4.42128	40.87432	79.52894	38.85592	77.71184	34.02456	68.04912	32.00616	60.41066	35.63928	53.50705
73	1.61472	3.22944	43.59744	84.97518	43.19376	86.38752	32.69808	65.39616	35.52384	65.81602	39.15696	58.32561
75	1.81656	3.585628	45.81768	91.63536	45.81768	91.63536	31.2852	62.5704	38.55144	70.04896	42.99192	63.6374
77	1.21104	2.200657	48.03792	96.07584	47.23056	94.46112	29.06496	58.12992	42.3964	78.44755	46.4232	68.95718
78	0.80736	1.393297	46.01952	92.03904	43.59744	87.19488	27.04656	54.09312	35.52384	66.36245	41.98272	62.3331
79	0.80736	1.393297	44.4048	88.8096	42.3864	84.7728	25.43184	50.86368	32.69808	61.9439	35.92752	53.3221
81	1.00704	1.792657	42.51264	85.02528	37.28208	74.56416	25.98768	51.97536	28.40976	54.99726	30.84048	45.80052
83	0.8052	1.436468	38.2092	76.4184	31.37688	62.75376	25.326	50.652	22.91688	45.83376	24.54888	36.84069
84	0.59904	1.19808	40.28256	80.56512	30.264	60.528	29.46096	58.92192	26.63088	53.26176	22.64592	34.29096
85	0.9984	1.9968	47.79264	95.58528	37.8	75.6	34.19712	68.39424	35.79024	71.58048	26.98704	40.28791
91	0.9984	1.9968	55.31136	110.6227	46.52544	93.05088	43.72992	87.45984	45.32736	90.65472	36.54144	54.9093
92	0.79872	1.59744	61.9008	123.8016	51.51744	103.0349	46.32576	92.65152	51.11808	102.2362	41.53344	61.7116
93	0.79872	1.59744	67.8912	135.7824	56.30976	112.6195	47.9232	95.8464	55.9104	111.8208	47.12448	70.29316
96	0.39936	0.79872	64.69632	129.3926	56.30976	112.6195	46.32576	92.65152	54.31296	108.6259	47.9232	71.42038
97	0	0	67.49184	134.9837	55.9104	111.8208	48.32256	96.64512	56.30976	112.6195	51.9168	77.86577
98	0.79872	1.59744	71.48544	142.9709	54.71232	109.4246	45.52704	91.05408	54.71232	109.4246	52.71552	78.7541
99	1.79712	3.59424	72.48384	144.9677	54.912	109.824	48.12288	96.24576	54.51264	109.0253	54.11328	82.10285
100	1.79712	3.59424	73.30816	146.6163	58.13248	116.265	52.53824	105.0765	58.53184	112.7031	56.53184	85.40045
103	2.19728	4.39456	77.73072	155.4614	61.75312	123.5062	57.35616	114.7123	61.35216	114.5926	56.9496	85.86574
105	2.19728	4.39456	73.76432	147.5286	62.57744	125.1549	61.38176	122.7635	57.37776	102.9314	51.77392	77.7186
106	2.19888	4.231867	69.0024	138.0048	63.40416	126.8083	61.80512	123.6102	52.60064	90.88697	46.19808	73.15636
107	1.40056	2.594762	69.83192	142.2751	65.82632	129.7818	64.22568	125.8523	53.0212	91.57892	43.41736	73.43565
110	1.40056	2.594762	69.83192	144.4454	64.22568	124.1128	63.42536	122.1474	49.0196	86.97897	38.61544	69.88586
113	1.0004	1.794442	76.63464	156.289	69.42776	131.3871	66.62664	125.8283	59.42376	110.5892	47.0188	90.78453
114	1.0004	1.794442	83.0372	168.2455	75.43016	142.5942	66.62664	125.1494	72.22888	138.9614	55.82232	111.9552
118	0.60024	1.06742	91.43656	183.4487	77.0308	144.6432	71.0284	130.1566	81.43256	155.97	66.22648	131.434
119	0.80032	1.438334	96.0384	187.8356	78.43136	147.7271	70.82832	131.0322	92.43696	175.7459	80.83232	162.407
121	2.0008	3.625997	101.2405	193.6348	81.23248	153.9035	72.82912	135.4609	106.0424	200.8845	98.83952	194.7478
124	2.40096	4.367606	98.0392	188.2575	75.23008	144.5322	68.42736	129.9233	106.0424	202.9036	104.8419	206.5406
125	3.601344	6.461299	103.6394	214.6471	79.62998	148.1929	77.2289	139.4536	109.2416	209.4336	104.4404	202.2538
126	4.801696	8.439747	106.0384	224.2417	86.83104	161.4549	86.83066	154.0871	121.6443	241.1755	103.6388	200.2506
133	5.201792	9.544413	115.6399	248.9866	99.23386	182.2826	102.0346	180.1693	128.0446	259.5141	102.8367	191.0996
134	4.001312	7.35675	122.4406	262.436	111.6367	200.6111	116.038	201.4827	134.4448	268.3794	98.03325	180.0528
135	3.601152	6.615141	135.2433	288.8299	121.6389	213.2706	129.2413	218.6634	141.2452	274.6638	99.63187	175.3732
139	2.600832	4.941346	138.6444	279.8994	124.6399	221.0473	125.4401	210.9351	143.4459	275.4681	109.0349	187.4691
140	1.800576	3.51253	123.8396	246.8243	129.4414	225.8801	127.0406	219.9566	129.0413	242.246	108.2346	187.1264
141	1.400448	2.381294	119.0381	231.0581	130.6418	234.0342	126.6405	219.7472	134.6431	243.952	111.8358	194.0509
152	2.00064	3.315445	126.8406	237.7086	129.2413	230.7534	122.4392	215.2089	136.8438	244.3436	126.0403	215.234
154	2.600832	4.270657	122.6392	218.2211	128.241	229.961	107.8345	191.5195	144.2461	253.9262	125.4401	215.2302
158	2.800896	4.651015	119.2381	212.811	120.4385	218.518	98.83162	182.3914	149.2477	268.3455	129.6415	234.5397
160	2.400768	4.05869	137.2439	243.9534	116.4372	209.6	94.43021	171.7556	146.0467	259.3872	123.2394	221.9439
161	2.00064	3.354652	139.6447	244.7771	114.0365	198.2067	85.22726	154.0049	126.8406	222.8617	116.0371	212.2201
162	1.800576	3.116124	128.241	232.4933	109.0349	196.094	88.22822	163.3034	115.4369	210.0883	104.6335	200.3035
165	1.800576	3.411311	115.0368	218.2679	96.63091	178.6685	87.02784	166.0095	93.42989	178.793	95.43053	190.8063
167	1.400448	2.611055	115.8371	218.4549	95.0304	177.0676	92.62963	182.5327	81.42605	153.6716	80.62579	160.3829
174	1.00032	1.946023	108.6348	208.1131	89.82874	176.3938	90.22886	188.3969	92.62963	178.7794	91.42925	181.1394

Table V.8
Sulfate Loading Rate in the Effluent (With Phosphate Addition)

Day	IAE	IIBE	IIIAE	IIIBE	IVAE	IVBE
	g/Day/m3	g/Day/m3	g/Day/m3	g/Day/m3	g/Day/m3	g/Day/m3
1	661.91	567.90	666.86	676.75	691.60	673.79
8	661.91	623.31	762.85	763.84	723.27	695.56
10	682.69	605.50	768.79	786.60	604.51	734.15
13	697.54	637.17	794.52	776.71	857.86	865.77
15	695.56	587.69	818.27	811.35	893.48	884.58
20	641.13	608.47	617.39	676.75	825.33	853.11
22	699.52	584.72	664.88	684.67	930.10	946.92
34	585.71	517.42	622.17	642.12	786.96	844.99
35	567.90	550.08	565.92	647.07	840.04	814.31
41	619.36	585.71	449.29	663.89	916.25	907.34
47	503.90	592.64	656.96	685.66	894.47	692.03
50	515.80	534.25	582.74	616.39	660.92	476.41
52	507.04	495.65	439.24	548.10	598.57	448.53
54	663.89	576.80	424.40	522.37	504.56	589.67
55	643.11	353.14	409.55	365.02	399.66	421.20
56	633.21	240.33	296.74	352.16	335.44	345.93
57	671.81	251.21	249.23	286.84	315.29	353.62
64	690.61	420.44	382.83	369.97	368.98	312.14
70	552.26	360.94	350.18	341.27	382.83	327.23
72	601.54	332.36	340.28	343.25	452.18	326.23
73	695.56	350.18	295.75	304.65	240.75	183.45
75	754.94	500.60	401.64	406.58	316.84	198.77
77	649.05	311.58	253.19	329.39	193.11	178.20
78	570.07	228.45	155.22	322.47	190.41	101.45
79	560.91	197.77	176.00	383.82	237.36	159.93
81	537.99	307.62	303.66	445.18	455.08	311.25
83	490.32	271.99	257.15	298.71	341.27	275.80
84	538.21	253.19	217.56	278.92	293.77	289.03
85	578.78	293.77	270.02	303.66	373.93	319.07
91	632.22	34.48	154.23	92.87	115.63	100.91
92	620.35	-10.05	39.43	65.16	14.69	88.89
93	673.79	14.69	43.39	80.01	47.35	67.04
96	689.62	82.97	124.54	192.82	86.93	102.46

97	643.11	78.03	141.36	179.96	134.44	76.28
98	666.86	107.72	157.20	203.71	151.26	146.90
99	745.04	-0.15	112.66	60.21	19.64	19.29
100	699.52	-29.84	56.25	50.32	11.72	-11.99
103	710.40	15.68	46.36	81.00	140.37	64.04
105	765.82	106.73	122.56	143.34	106.62	117.35
106	737.12	123.55	117.61	109.69	166.19	226.26
107	811.35	128.50	108.71	59.22	213.04	208.75
110	700.64	90.89	60.21	99.80	263.87	422.42
113	719.51	66.39	116.50	130.73	229.79	433.74
114	629.67	69.61	88.81	146.64	307.74	469.37
118	604.66	-21.98	-18.25	47.85	-20.50	40.55
119	583.75	-23.40	-13.71	68.62	-20.49	22.13
121	657.09	-21.12	29.40	32.24	104.88	23.68
124	611.48	-15.11	105.52	157.88	-9.50	-11.83
125	645.49	-13.99	141.96	179.79	-6.60	-9.37
126	691.30	23.12	289.83	304.71	37.32	44.46
133	932.83	30.20	115.51	-12.35	67.04	393.42
134	896.77	-27.61	34.63	58.83	27.95	428.45
135	1228.80	-18.98	-15.22	32.68	54.20	213.60
140	1091.49	-15.01	94.58	122.34	-16.96	75.80
141	1160.92	67.46	131.96	289.45	90.05	116.96
152	1138.07	1160.58	122.42	415.22	1042.98	910.88
154	1444.26	470.21	315.60	399.60	153.12	463.23
158	1207.46	286.58	343.60	592.09	7.20	121.24
161	1548.62	624.30	778.69	1132.98	292.78	309.60
165	1235.73	455.32	463.11	739.33	806.36	829.16
167	1346.14	793.81	782.22	520.46	862.39	674.04

Table V.9
Sulfate Loading Rate in the Influent (With Phosphate Addition)

Day	IAi	IIBi	IIIAi	IIIBi	IVAi	IVBi
	g/Day/m3	g/Day/m3	g/Day/m3	g/Day/m3	g/Day/m3	g/Day/m3
1	661.91	661.91	776.71	776.71	838.07	838.07
8	672.80	672.80	801.45	801.45	836.09	836.09
10	699.52	699.52	841.03	841.03	839.05	839.05
13	664.88	664.88	814.31	814.31	952.86	952.86
15	695.56	695.56	874.68	874.68	972.66	972.66
20	691.60	691.60	633.52	699.52	878.21	878.21
22	686.65	686.65	737.12	737.12	987.50	987.50
34	585.71	585.71	635.98	683.68	846.80	910.31
35	569.87	569.87	687.64	687.64	899.42	899.42
41	621.34	621.34	616.75	703.47	972.66	972.66
47	506.26	639.15	715.35	715.35	926.14	733.58
50	499.28	628.26	632.22	632.22	609.46	464.35
52	520.37	656.96	624.30	624.30	622.33	436.72
54	676.75	676.75	625.29	625.29	665.87	665.87
55	651.02	651.02	643.11	643.11	630.24	481.71
56	629.25	629.25	585.71	585.71	602.23	514.19
57	657.95	657.95	633.21	633.21	586.87	488.90
64	619.36	619.36	561.96	561.96	597.58	471.39
70	534.79	548.73	634.20	634.20	568.88	427.67
72	624.30	624.30	624.30	624.30	542.11	430.06
73	649.05	649.05	599.56	599.56	555.63	461.42
75	771.76	771.76	649.05	649.05	604.85	493.76
77	615.40	615.40	616.39	616.39	537.35	442.35
78	514.18	582.74	590.66	590.66	537.51	432.78
79	517.69	604.51	583.73	583.73	606.49	445.81
81	515.19	626.28	578.78	578.78	607.48	466.17
83	467.80	555.03	562.95	562.95	553.05	416.74
84	592.64	592.64	558.00	558.00	583.73	442.99
85	605.50	605.50	538.21	538.21	571.85	433.98
91	612.43	612.43	570.86	570.86	593.63	445.57
92	622.33	622.33	576.80	576.80	600.55	439.09
93	677.74	677.74	613.42	613.42	650.03	495.66

96	677.74	677.74	602.53	602.53	674.78	482.34
97	662.90	662.90	603.52	603.52	660.92	505.16
98	682.69	682.69	633.21	633.21	668.84	499.29
99	666.86	666.86	652.01	652.01	694.57	523.79
100	672.80	672.80	655.97	655.97	682.69	512.02
103	661.91	661.91	628.26	628.26	669.83	523.22
105	723.27	723.27	600.55	600.55	555.78	500.03
106	704.46	704.46	640.14	640.14	586.19	509.60
107	770.77	770.77	686.65	686.65	563.52	511.90
110	644.76	719.31	646.08	646.08	589.10	704.46
113	634.12	765.24	598.69	576.40	729.97	803.80
114	638.56	770.61	556.44	562.06	637.15	693.43
118	582.23	665.30	627.37	627.37	645.23	645.23
119	587.96	675.96	602.35	602.35	643.03	643.03
121	582.70	634.61	598.40	549.45	579.20	630.80
124	602.45	623.56	574.00	574.00	638.52	724.03
125	587.78	601.48	598.71	598.71	634.70	634.70
126	724.31	766.02	703.95	735.17	788.85	755.35
133	916.43	1345.07	894.85	845.10	1021.37	905.21
134	886.80	1127.23	968.89	856.08	1149.39	1037.50
135	1208.38	1113.17	910.71	910.71	1087.04	922.24
140	1091.49	952.67	917.59	917.59	978.95	902.89
141	1172.34	1090.34	964.67	826.45	1052.13	901.38
152	1179.28	1479.54	1274.59	1394.15	1449.85	1498.08
154	1401.60	1502.39	1471.39	1328.14	1372.95	1372.95
158	1169.73	1237.12	1191.51	1300.80	1259.92	1259.92
161	1509.04	1509.04	1425.91	1425.91	1496.17	1496.17
165	1209.60	1322.94	1327.27	1327.27	1299.12	1536.75
167	1350.44	1516.29	1442.89	1442.89	1550.10	1550.10

Table V.10
Lactate Loading Rate (With Phosphate Addition)

DAY	IAE	IIBE	IIIAE	IIIBE	IVAE	IVBE
	Kg/Day/m3	Kg/Day/m3	Kg/Day/m3	Kg/Day/m3	Kg/Day/m3	Kg/Day/m3
52	1.58	2.00	2.00	2.00	2.00	1.40
54	2.00	2.00	2.00	2.00	2.00	2.00
55	2.00	2.00	2.00	2.00	2.00	1.53
56	2.00	2.00	2.00	2.00	1.88	1.60
57	2.00	2.00	2.00	2.00	1.89	1.57
64	2.00	2.00	2.00	2.00	2.00	1.58
70	1.68	1.73	2.00	2.00	2.00	1.50
72	2.00	2.00	2.00	2.00	1.80	1.43
73	2.00	2.00	2.00	2.00	1.82	1.51
75	2.00	2.00	2.00	2.00	1.83	1.49
77	2.00	2.00	2.00	2.00	1.82	1.50
78	1.76	2.00	2.00	2.00	1.81	1.46
79	1.71	2.00	2.00	2.00	2.00	1.47
81	1.65	2.00	2.00	2.00	2.00	1.53
83	1.69	2.00	2.00	2.00	2.00	1.51
84	2.00	2.00	2.00	2.00	2.00	1.52
85	2.00	2.00	2.00	2.00	2.00	1.52
91	3.00	3.00	3.00	3.00	3.00	2.25
92	3.00	3.00	3.00	3.00	3.00	2.19
93	3.00	3.00	3.00	3.00	3.00	2.29
96	3.00	3.00	3.00	3.00	3.00	2.14
97	3.00	3.00	3.00	3.00	3.00	2.29
98	3.00	3.00	3.00	3.00	3.00	2.24
99	4.00	4.00	4.00	4.00	4.00	3.02
100	4.00	4.00	4.00	4.00	4.00	3.00
103	4.00	4.00	4.00	4.00	4.00	3.12
105	4.00	4.00	4.00	4.00	3.32	2.99
106	4.00	4.00	4.00	4.00	3.40	2.95
107	4.00	4.00	4.00	4.00	3.23	2.93
110	3.59	4.00	4.00	4.00	3.34	4.00
113	3.60	4.34	3.71	3.57	3.97	4.37
114	3.60	4.34	3.56	3.60	3.78	4.12

118	5.04	5.76	5.49	5.49	5.88	5.88
119	5.11	5.87	5.87	5.87	5.87	5.87
121	5.31	5.78	5.78	5.31	5.31	5.78
124	5.48	5.67	5.67	5.67	5.67	6.43
125	5.47	5.59	5.59	5.59	5.59	5.59
126	5.56	5.88	5.88	6.14	6.14	5.88
133	5.23	7.68	5.23	4.94	5.90	5.23
134	5.03	6.40	5.70	5.03	6.31	5.70
135	6.88	6.34	5.38	5.38	6.34	5.38
139	6.88	5.69	5.05	5.05	5.27	5.27
140	6.88	6.01	4.95	4.95	5.37	4.95
141	6.30	5.86	5.52	4.73	5.52	4.73
152		5.91	6.98	5.72	5.72	5.91
154		5.66	8.03	5.43	5.43	5.43
158		4.94	6.58	5.39	4.94	4.94
160			6.76	6.76	8.45	8.45
161			8.00	8.00	10.00	10.00
162			6.65	7.25	8.31	9.87
165			7.00	7.00	8.45	10.00
167			7.81	7.81	9.76	9.76

Table V.11
Total Organic Carbon (With Phosphate Addition)

DAY	IIi	IIIi	IVi	IIBE	IIIAE	IIIBE	IVAE	IVBE
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	251.50	250.40	254.50	204.40	213.50	220.70	229.40	216.00
8	159.78	176.03	171.99	139.79	132.35	130.54	144.24	151.77
13	244.28	258.52	262.20	200.38	222.57	208.67	238.91	234.07
15	261.40	265.07	261.41	226.92	218.90	199.15	239.97	236.24
20	264.94	235.81	261.25	239.33	206.59	208.68	235.63	231.90
22	223.47	234.55	254.35	241.28	206.84	219.34	236.89	243.69
50	210.10	250.89	252.75	204.71	198.48	207.28	229.70	221.03
52	139.64	256.70	264.42	124.58	190.18	198.12	203.93	209.53
54	108.95	154.21	271.52	76.64	129.65	126.19	201.13	200.81
78	45.83	33.43	62.47	37.80	49.22	103.67	40.55	93.92

V.3 Heavy Metals

Table V.12
pH Values During Heavy Metal Studies

DAY	IAE	IIBE	IIIAE	IIIBE	IVAE	IVBE	Influent	IAE metal	IIIA metal	IIIB metal	IVA metal	IVB metal
256	8.06	7.72	7.82	8.12	8.02	7.88	8.89	1.72	1.76	1.62	1.74	1.71
258	6.96	7.2	7.13	7.46	7.37	7.47	7.52	1.73	1.77	1.6	1.73	1.7
260	6.85	8.11	7.28	7.39	7.17	7.17	7.39	1.78	1.91	1.71	1.83	1.8
263	6.7	7.78	7.16	7.12	6.97	7.05	7.03	1.62	1.69	1.63	1.62	1.64
265	6.59	7.17	7.09	7.11	6.77	6.83	6.8	1.61	1.48	1.43	1.6	1.61
267	6.53	7.78	6.94	7.22	6.87	7.05	7.7	1.43	1.32	1.36	1.55	1.59
270	6.42	8.12	7.41	7.21	7.05	7	7.65	1.59	1.56	1.15	1.65	1.7
272	6.23	7.73	6.91	7.23	6.98	6.9	7.26	1.55	1.53	1.2	1.65	1.71
277	4.98	6.99	7.08	6.83	6.74	6.9	6.95	1.3	1.35	1.2	1.45	1.45
279	4.71	7.32	6.88	6.7	6.66	6.68	6.74	1.15	1.19	1.1	1.37	1.37
284	4.62	7.86	7.36	6.9	6.69	6.48	7.47	1.13	1.47	1.06	1.51	1.64
286	4.51	7.52	7.96	6.42	6.3	6.53	7.34	1.36	1.12	1.29	1.76	1.88
292	3.38	7.03	7.21	5.26	4.87	5.85	7.34	0.98	0.69	0.99	1.09	1.17

Table V.13
Sulfate Loading Rate During Heavy Metal Studies

DAY	IAE g/day/m3	IIBE g/day/m3	IIIAE g/day/m3	IIIBE g/day/m3	IVAE g/day/m3	IVBE g/day/m3	IAi g/day/m3	IIBi g/day/m3	IIIAi g/day/m3	IIIBi g/day/m3	IVAi g/day/m3	IVBi g/day/m3
223	1133.333	56.35627	790.0653	881.8849	569.1097	526.2626	942.6131	709.3264	718.1213	755.6759	748.5691	752.9892
226	1034.391	50.1441	706.7269	836.2321	668.9641	537.9909	947.7137	799.2362	838.9557	857.9531	878.3805	879.6263
228	1011.726	52.88205	693.1041	778.6354	624.117	538.2028	969.6145	902.6569	930.3462	951.447	1001.886	992.4604
256	979.9654	71.84407	643.7755	683.3802	606.6445	510.2863	993.5003	915.0714	975.522	949.8273	1013.605	1013.432
258	989.5458	92.60665	484.9807	623.375	597.9702	476.0416	1040.145	915.3389	979.4478	957.138	1026.974	1028.723
260	1004.515	98.11959	452.2101	552.3972	543.9514	444.0377	1076.206	915.6534	981.886	943.6804	1027.931	1033.008
263	1051.889	144.6989	491.1821	535.6233	477.8795	422.0481	1095.358	930.4784	976.0162	953.8262	1033.483	1039.523
265	1026.688	163.453	502.4629	519.0744	448.7044	392.033	1105.863	918.7109	974.2075	966.6849	1027.34	1034.787
267	1036.364	158.6356	471.3037	511.2346	415.7423	380.5541	1137.147	923.4919	981.142	979.3672	1035.25	1031.752
270	1082.193	159.1013	434.3418	532.1888	451.4121	385.5487	1149.995	924.0596	942.1954	981.0089	1069.751	1027.955
272	1233.65	192.2878	370.8977	665.1631	554.2107	483.6275	1297.326	934.1619	923.0295	1035.734	1116.492	1078.177
277	1423.715	186.6763	308.3307	787.1184	683.8933	582.0128	1473.552	915.5046	900.6871	1075.736	1158.357	1130.646
284	1889.664	205.4641	337.5788	963.5156	969.3816	728.7832	1969.337	934.8901	909.7	1164.129	1332.939	1309.057
286	2209.464	229.9371	386.5305	1153.33	1240.24	895.5355	2429.344	919.0414	892.7664	1253.428	1461.636	1477.234
292	2482.169	253.3879	454.544	1319.232	1389.562	1066.621	2898.367	912.6735	905.8232	1358.176	1576.378	1657.749
294	2662.848	247.1954	533.7414		1481.564	1127.47	3242.953	6.5078	904.4606		1673.622	1778.646

Table V.14
Excess Sulfide Concentration During Heavy Metal Studies

DAY	IIBE mg/L	IIIAE mg/L	IIIBE mg/L	IVAE mg/L	IVBE mg/L
241	109.51	66.18	69.79	42.92	80.63
243	109.10	68.59	71.40	50.94	100.68
248	97.01	70.11	54.95	45.28	96.60
249	96.09	72.42	46.87	50.01	94.92
256	108.42	79.56	50.43	60.77	97.24
258	105.30	80.49	47.77	64.92	91.33
260	104.39	82.43	43.31	71.66	84.83
263	110.38	72.45	48.90	72.85	82.04
265	108.98	61.48	47.11	73.85	83.83
267	105.79	61.88	43.51	72.26	81.84
270	106.39	62.47	37.33	71.26	76.85
272	101.20	64.47	33.73	62.08	69.66
277	106.46	74.51	30.55	56.11	60.49
279	106.34	79.14	25.97	39.94	45.13
284	106.60	62.98	21.79	26.17	30.96
286	105.87	49.41	18.80	15.80	17.79
292		35.84	15.81	10.21	9.01
294		19.02		6.20	7.41

Table V.15
Heavy Metal Concentration in the Influent

	IIIai		IIIbi		IVai		IVbi	
	Pb		Cr		Cu		Cd	
Day	Dissolved mg/L	Total mg/L	Dissolved mg/L	Total mg/L	Dissolved mg/L	Total mg/L	Dissolved mg/L	Total mg/L
256	2.67		3.79		5.31		10.83	
258	2.84	2.90	4.09	4.68	5.63	8.88	11.83	11.37
260	2.93		4.19		5.70		12.04	
263	2.79		6.87		12.24		23.71	
265	3.26	3.60	7.34	8.68	12.07	14.71	22.57	22.43
267	3.21		7.70		11.73		21.86	
270	4.29		16.43		28.43		46.86	
272	4.01	4.24	21.43	21.86	25.29	29.14	50.43	51.33
277	5.17	5.03	48.00	48.00	58.29	56.14	124.14	109.14
279	5.80		47.57		60.29		132.29	
284	6.84	6.77	78.00	87.14	110.00	116.43	235.71	240.00
286	9.00		87.71		174.29		262.86	
292	16.29		106.57		351.43		541.43	
294	18.43	17.43			388.57	394.29	608.57	554.29

Table V.16
Heavy Metal Concentration in the Influent Control

Iai							
Cd		Pb		Cu		Cr	
Dissolved mg/L	Total mg/L	Dissolved mg/L	Total mg/L	Dissolved mg/L	Total mg/L	Dissolved mg/L	Total mg/L
10.76		0.90		4.94		3.61	
11.51	10.80	0.94	2.96	7.19	8.21	4.04	4.07
11.81		0.96		7.39		4.27	
24.00		0.67		12.24		6.99	
23.14	23.43	0.87	0.81	14.06	14.43	7.47	7.60
23.00		0.87		14.06		7.47	
49.14		0.52		29.14		14.86	
53.00	53.86	0.35	0.47	26.57	28.60	19.29	18.60
134.57	134.57	0.49	0.49	57.29	55.28	42.14	41.70
142.86		0.47		58.14		43.29	
250.00	210.00	0.00	0.87	121.00	106.43	80.57	73.14
277.14		0.47		175.71		92.43	
580.00		0.10		352.86		106.14	
675.71	637.14	0.00	0.00	411.43	412.86	122.00	123.00

Table V.17
Heavy Metal Concentration in Reactor IIIA and IIIB (Effluent)

IIIac					IIIbc				
Pb					Cr				
Dissolved		Total		S2 excess	Dissolved		Total		S2 excess
mg/L	%removal	mg/L	%removal	mg/L	mg/L	%removal	mg/L	%removal	mg/L
0.23	91.35			79.56	1.33	64.87			50.43
0.06	97.78	1.15	60.34	80.49	1.16	71.61	1.11	76.32	47.77
0.11	96.38			82.43	0.80	80.84			43.31
0.24	91.31			72.45	1.11	83.85			48.90
0.13	95.95	1.37	61.94	61.48	1.11	84.88	1.39	83.99	47.11
0.11	96.58			61.88	0.42	94.53			43.51
0.13	96.97			62.47	0.87	94.72			37.33
0.01	99.80	1.37	67.69	64.47	1.86	91.32	2.34	89.30	33.73
0.48	90.64	1.85	63.22	74.51	6.92	85.58	8.78	81.71	30.55
0.08	98.69			79.14	8.47	82.20			25.97
0.30	95.60	2.78	58.95	62.98	24.80	68.21	32.00	63.28	21.79
0.14	98.41			49.41	50.50	42.43			18.80
0.27	98.36			35.84	97.60	8.42			15.81
0.00	100.00	5.70	67.30	19.02					0.00

Table V.18
Heavy Metal Concentration in Reactor IVA and IVB (Effluent)

IVae					IVbe				
Cu					Cd				
Dissolved		Total		S2 excess	Dissolved		Total		S2 excess
mg/L	%removal	mg/L	%removal	mg/L	mg/L	%removal	mg/L	%removal	mg/L
0.11	97.87			60.77	0.20	98.17			97.24
0.14	97.49	0.65	92.70	64.92	0.11	99.07	3.50	69.22	91.33
0.19	96.72			71.66	0.12	99.03			84.83
0.18	98.50			72.85	0.07	99.70			82.04
0.06	99.50	1.31	91.07	73.85	0.00	100.00	8.20	63.44	83.83
0.05	99.54			72.26	0.02	99.90			81.84
0.07	99.75			71.26	0.02	99.97			76.85
0.00	100.00	6.26	78.52	62.08	0.00	100.00	13.74	73.28	69.66
0.00	100.00	4.84	91.33	56.11	0.00	100.00	67.80	37.88	60.49
0.00	100.00			39.94	0.00	100.00			45.13
0.00	100.00	7.28	93.75	26.17	0.00	100.00	194.80	18.83	30.96
4.07	97.66			15.80	0.26	99.90			17.79
27.00	92.32			10.21	5.70	98.95			9.01
11.10	97.14	21.80	94.47	6.20	0.00	100.00	29.40	94.70	7.41

Table V.19
Heavy Metal Concentration in Control Reactor (Effluent)

Iac							
Cd				Pb			
Dissolved		Total		Dissolved		Total	
mg/L	%removal	mg/L	%removal	mg/L	%removal	mg/L	%removal
18.20	0.00			0.09	89.90		
9.56	16.97	10.28	4.81	0.05	94.44	0.47	84.12
9.56	19.08			0.06	93.32		
14.10	41.25			0.10	85.26		
6.28	72.86	10.08	56.98	0.07	91.85	0.12	84.94
0.01	99.98			0.05	94.38		
0.05	99.89			0.04	91.73		
0.00	100.00	19.96	62.94	0.00	100.00	0.00	100.00
130.00	3.40	111.00	17.52	0.07	86.16	0.00	100.00
120.00	16.00			0.00	100.00		
167.00	33.20	164.60	21.62	0.00	0.00	0.17	80.03
201.00	27.47			0.00	100.00		
643.00	0.00			0.10	0.00		
496.00	26.60	425.00	33.30	0.00	0.00	0.00	0.00

Cu				Cr			
Dissolved		Total		Dissolved		Total	
mg/L	%removal	mg/L	%removal	mg/L	%removal	mg/L	%removal
1.21	75.52			0.41	88.77		
0.75	89.62	3.62	55.91	1.00	75.36	2.16	46.93
0.75	89.82			1.17	72.61		
0.01	99.89			2.64	62.21		
0.00	100.00	2.80	80.60	3.32	55.56	3.36	55.79
0.00	100.00			1.30	82.60		
0.00	100.00			4.65	68.70		
0.00	100.00	1.04	96.36	11.00	42.96	10.30	44.62
45.90	19.88	47.20	14.62	33.60	20.27	32.40	22.30
47.10	18.99			30.30	30.00		
52.40	56.69	55.80	47.57	35.90	55.44	43.60	40.39
84.40	51.97			57.20	38.11		
389.00	-10.24			131.00	0.00		
277.00	32.67	266.00	35.57	97.10	20.41	82.90	32.60

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